Suppression of the large Zeeman splitting of the states of impurity donor–acceptor pairs in semimagnetic semiconductors

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The edge photoluminescence of donor-acceptor (DA) pairs in crystalline $Zn_{1-x}Mn_xSe$ has been investigated experimentally. A decrease in the large Zeeman splitting of the states of the DA pairs, especially the hole states of the DA pairs, relative to the splitting of the free-exciton states in the same crystal has been noted. Detailed treatment of the experimental results has revealed that this decrease cannot be attributed to the absence of Mn^{2+} ions near the deep impurity centers or to the realization of a magnetic polaron effect. The decrease in the large Zeeman splitting of the DA pairs in $Zn_{1-x}Mn_xSe$ has been explained in the framework of a model of a two-parameter impurity center. The exchange interaction has been calculated in this model, and it has been shown that this interaction is weakened significantly owing to the fact that it does not involve most of the impurity-center wave function which is concentrated within its small (atomic) radius. The weakening of the exchange interaction is responsible for the decrease in the Zeeman splitting. Good agreement between the theoretical and experimental curves has been obtained.

1. INTRODUCTION

It has been reported[1–3] that semimagnetic semiconductors of the type $A^{II}_{1-x}M_xB^{IV}$ (M=Mn, Fe, ...) exhibit large Zeeman splitting of free-exciton states in a magnetic field. This effect is a consequence of the exchange interaction of the free carriers with the localized $3d$ electrons of the transition metal ions. In such a case the effective field acting on the spin of each electron (hole) is many times greater than the external magnetic field. It has been noted[4,5] that the large Zeeman splitting for free carriers, free excitons, and excitons bound in shallow donors is of approximately the same magnitude, while the magnitude of the splitting of hole states is much smaller for excitons in acceptor centers—which are characterized by significant binding energies in $A^{II}B^{IV}$ compounds—than for free excitons. This decrease in the large Zeeman splitting was attributed in Ref. 4 to the fact that in samples of $Cd_{1-x}Mn_xTe$ with $x \ll 1$, there are generally no Mn^{2+} ions near a deep acceptor center within a radius specified by the Bohr radius of the center. Thus, the concentration of these ions in the regions where most of the acceptors are localized is considerably smaller than the mean concentration throughout the crystal.

As was noted in Ref. 5 in an investigation of samples with a comparatively large content of Mn^{2+} ions, another reason for the weakening of the large Zeeman splitting may be the realization of a magnetic polaron effect, which results in the spontaneous magnetization of the magnetic ions found within the Bohr radius of donor and acceptor centers.

In this communication we present the results of magneto-optical investigations of a crystal of $Zn_{1-x}Mn_xSe$ ($x=0.008$). The recombinational photoluminescence bands of donor-acceptor (DA) pairs were studied. It was discovered that the magnitude of the splitting of the hole states of DA pairs, as in the case of excitons in neutral acceptors, is significantly smaller than that for free excitons. The mean distance between Mn^{2+} ions for the values of x considered is at most comparable to the Bohr radii of the donors and acceptors. Under such conditions there should be no decrease in the large Zeeman splitting due to the absence of magnetic Mn^{2+} ions within the Bohr radius of most of these states. In addition, there is probably no magnetic polaron effect here, since the positions and widths of the corresponding spectral lines differ only slightly from those for the original pure crystal of ZnSe and since there is no specific temperature dependence for the parameters characterizing these lines.

The observed decrease in the splitting of the levels under magneto-optical effects in the present work can be explained using a model of a two-parameter impurity center,[6] in which it is assumed that sufficiently deep hole (electron) states have a nonhydrogen-like character and the wave function of each state is described by two characteristic radii, one of which is of an atomic scale, while the other has a form typical of states with a large radius $r_0=\hbar/\sqrt{2m^*\varepsilon_0}$, where ε_0 is the energy of the state measured from the band edge and m^* is the effective mass of the carrier in the band. Here the portion of the wave function which is concentrated within the atomic (small) radius does not participate in the exchange interaction, since there are no magnetic atoms within this radius.

2. EXPERIMENTAL RESULTS

The measurements were performed on the same sample of a cubic crystal of $Zn_{1-x}Mn_xSe$ ($x=0.008$) and under the same conditions ($T=2$ K, $H \leqslant 3$ T) as in Ref. 3, where the magneto-optical effects were studied for the free-

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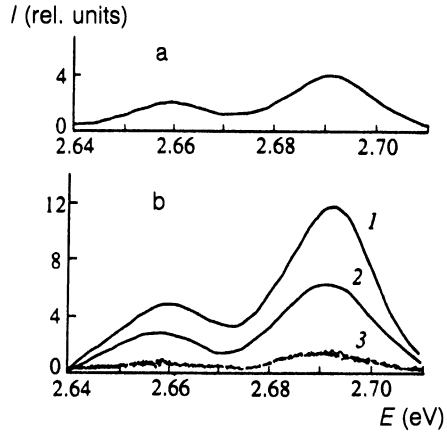

FIG. 1. Photoluminescence lines of DA pairs in a $Zn_{1-x}Mn_xSe$ crystal: a) in the absence of a magnetic field; b) lines of different polarization in a magnetic field $H=1$ T.

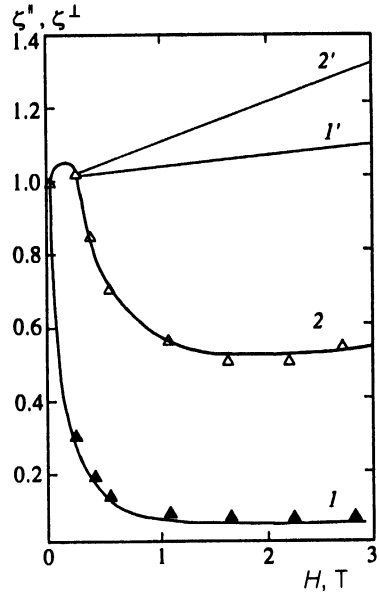

FIG. 2. Dependence of $\zeta^{\parallel}$ (△) and $\zeta^{\perp}$ (▽) in $Zn_{1-x}Mn_xSe$ and ZnSe crystals on the magnetic field.

exciton reflection band. The luminescence was excited by the $\lambda_{exc}=3650$ Å resonance line of a mercury gas-discharge lamp. The spectroscopic measurements were performed on a DFS-12 spectrometer with slit width $\leqslant 0.5$ Å. The magnetic field was produced by a superconducting solenoid with a cross section that permits the performance of measurements in the longitudinal ($\mathbf{k}\parallel \mathbf{H}$) and transverse ($\mathbf{k}\perp \mathbf{H}$) geometries of an ($\mathbf{H}\parallel \mathbf{z}$) experiment. The emission was detected in two circular polarizations of the light wave for $\mathbf{k}\parallel \mathbf{H}$ (σ^+: $E^+=E_x-iE_y\neq 0$, $E_z=0$ and σ^-: $E^-=E_x+iE_y$, $E_z=0$) and in two linear polarization for $\mathbf{k}\perp \mathbf{H}$ (σ : $E_x\neq 0$, $E_y=0$, $E_z=0$ and π : $E_x=E_y=0$, $E_z\neq 0$). Here $\mathbf{k}$ is the wave vector, and $\mathbf{E}$ is the electric field-strength vector of the light wave.

Figure 1a shows the photoluminescence spectrum of the sample studied in the present work. It consists of two resonance bands formed as a result of DA pair recombination. The intense band with a higher energy corresponds to zero-phonon recombination, and the other band is a Stokes replica of the first band. The distance between the maxima of these bands $h\nu=31\pm 2$ meV is approximately equal to the quantum energy of an LO phonon in ZnSe.[7] We note that the complete photoluminescence spectrum of the sample also contains a group of narrower recombination lines of various exciton states located in the immediate vicinity of the free-exciton reflection line ($E\approx 2.89$ eV), which are not shown in Fig. 1a. In addition, the spectrum displays a broader band of intracenter transitions of the Mn^{2+} ions at longer wavelengths.

We stress that the spectral positions of these exciton and DA pair bands in $Zn_{1-x}Mn_xSe$ scarcely differ from those observed for pure ZnSe. This means that the energies of the states responsible for these photoluminescence bands do not change significantly in response to the incorporation of Mn^{2+} ions in the ZnSe lattice. Moreover, these bands do not shift or broaden when the temperature of the sample changes from 2 K to 4.2 K.

Figure 1b presents a picture of the photoluminescence spectrum, which shows how a magnetic field $H=1$ T influences the DA pair bands in the σ^+ (curve *1*), π (curve *2*), and σ^- (curve *3*) polarizations. It can be seen that a comparatively strong field alters the intensity of the polarized emission, but does not cause appreciable shifts or splitting of the polarized DA pair bands. Other measurements performed for $H>1$ T and up to $H=3$ T likewise did not reveal any changes in the spectral positions of the maxima of the observed resonance lines with an absolute value exceeding the measurement error $\Delta E^{err}=2$ meV, i.e., $|\Delta E^{\pm\sigma,\pi}(\mathbf{H})|\leqslant\Delta E^{err}$, where $\Delta E^{\pm\sigma,\pi}(\mathbf{H})=E^{\pm\sigma,\pi}(\mathbf{H})-\mathrm{E}(0)$ and $E^{\pm\sigma,\pi}(\mathbf{H})$ denotes the positions of the band maxima. For comparison, we note that in the band due to the reflection of light by free excitons, the splitting between the outermost components with σ^+ and σ^- polarizations amounts to 19 meV when $H=1$ T, while the splitting between the two π-polarized components equals 8 meV. If the splitting of the DA pair bands were of the same or comparable magnitude, it would have been clearly displayed in Fig. 1b. This splitting would also have exceeded the measurement error and the half-width of the band. We therefore conclude that the splitting of the DA pair bands is many times weaker than that observed in the free-exciton band.

To determine the parameters of the splitting of the electron and hole states associated with the DA pairs when $H\neq 0$, we performed detailed measurements of the polarization characteristics of the DA pair emission. The results of these measurements are presented in Fig. 2, where the triangles and inverted triangles refer to the values of the ratios $\zeta^{\parallel}(\mathbf{H})=I^{-\sigma}(\mathbf{H})/I^{+\sigma}(\mathbf{H})$ and $\zeta^{\perp}(\mathbf{H})=I^{\pi}(\mathbf{H})/I^{\sigma}(\mathbf{H})$, respectively, in the longitudinal ($\mathbf{k}\parallel \mathbf{H}$) and transverse ($\mathbf{k}\perp \mathbf{H}$) geometries of the experiment. Here $I^{\pm\sigma}(\mathbf{H})$ denotes the intensity of the emission with circular $\sigma^{\pm}$ polarization, and $I^{\pi,\sigma}(\mathbf{H})$ denotes the intensity of the emission with linear π and σ polarizations at the maximum of the zero-phonon photoluminescence band. The plots of the

dependence of $\zeta^{\parallel}$ (**H**) and $\zeta^{\perp}$ (**H**) on the field observed for the band of the phonon replica are not shown, since they do not differ significantly from the plots shown in Fig. 2. Curves *1* and *2* correspond to the results of a theoretical treatment of the experimental data, and will be discussed below. Lines *1′* and *2′* are calculated curves based on experimental data from Ref. 8 (the g factors have the same value as in the present work), and they illustrate the variation of the values of $\zeta^{\parallel}$ and $\zeta^{\perp}$ corresponding to the DA pairs in a pure crystal of ZnSe in a magnetic field. Qualitative and quantitative differences in the behavior of these parameters for the ZnSe and $Zn_{1-x}Mn_xSe$ crystals are readily apparent. This is clearly a consequence of the interaction of the electrons and holes bound in the DA pairs with the subsystem of Mn^{2+} ions in $Zn_{1-x}Mn_xSe$.

3. ANALYSIS AND TREATMENT OF EXPERIMENTAL RESULTS

We note above all that in the present experiment, as in Ref. 3, the spectral positions of the edge photoluminescence and exciton reflection bands for $Zn_{1-x}Mn_xSe$ are essentially the same as those for ZnSe.[8–10]. Hence it may be concluded that the energy spectrum of the band states, as well as the impurity levels responsible for these bands, does not undergo appreciable changes due to the presence of Mn^{2+} ions in the lattice. Therefore, we shall assume that the DA pair bands recorded for $Zn_{1-x}Mn_xSe$ result, as in ZnSe, from the recombination of electrons ($s_e=1/2$) localized at the donors D (their binding energy is $\varepsilon_b=28$ meV) and holes ($s_h=3/2$) localized at the acceptors A ($\varepsilon_b=80$ meV). Here it is assumed that the spin states of the electrons localized at donors and of the holes localized at acceptors coincide with the corresponding values for the spins of the free carriers. Therefore, the values of s_e, the spin of an electron from the lower s-type Γ_6 band, and of s_h, the effective spin of a hole from the upper p-type Γ_8 valence subband,[11] are given along with the binding energies ε_b of the localized states.[8,10]

In a magnetic field $H=H_z\neq 0$, $H_x=H_y=0$, the Γ_6 and Γ_8 bands split into spin subbands with $s_e^z=\pm 1/2$ and $s_h^z=\pm 1/2$, $\pm 3/2$. The magnitude of this splitting is determined mainly by the effect exerted on the spin s_e (s_h) of an electron (hole) by the exchange field[3]

$$G_{e(h)}(\mathbf{H})=I_{e(h)}x\langle \mathbf{s}_{Mn}\rangle_{\mathbf{H},T}, \tag{1}$$

which depends on the magnitude and sign of the constant $I_{e(h)}$ of the s–d (p–d) exchange interaction of a current carrier $e(h)$ with $3d$ electrons of Mn^{2+} ($s_{Mn}=5/2$), where x is the concentration of Mn^{2+} ions, and $\langle s_{Mn}\rangle_{H,T}$ is the mean value of their spins in the $Zn_{1-x}Mn_xSe$ sample when $\mathbf{H}\neq 0$. Exchange field (1) determines the large Zeeman splitting for free excitons and excitons bound in shallow centers.

The exchange interaction of electrons (holes) bound in relatively deep impurity centers with Mn^{2+} has some special features, which will be examined in detail below (Sec. 3). In treating the experimental data we shall, nevertheless, assume that the Zeeman splitting of the donor levels [$\Delta E_e(\mathbf{H})$] and of the acceptor levels [$\Delta E_h(\mathbf{H})$] may be represented in similar forms

$$\Delta E_e(\mathbf{H})=G_e^*+g_e\beta H,$$
$$\Delta E_h(\mathbf{H})=G_h^*+g_h\beta H. \tag{2}$$

Here $G^*_{e(h)}(\mathbf{H})=G_{e(h)}P_{e(h)}$ is the exchange field acting on the spin $\mathbf{s}_e(\mathbf{s}_h)$ in the states indicated; $P_{e(h)}$ is the reduction parameter, which depends on the model of the impurity center and the depth of the impurity level; $g_{e(h)}$ is the g factor of an electron in a donor (hole in an acceptor); β is the Bohr magneton.

The Zeeman effect for the analogous band of a DA pair in a pure ZnSe crystal was investigated in detail in Ref. 8. As in Ref. 8, the splitting of this band was not detected at $H\leqslant 6$ T due to its large width ($\Gamma\simeq 7$ meV). At the same time, we were able to detect changes in the polarization characteristics of the luminescence, whose theoretical treatment makes it possible to determine the values $g_e=1.2$ and $g_h=0.4$. This suggests that the values of g_e and g_h for the $Zn_{1-x}Mn_xSe$ sample studied are the same as those for a pure ZnSe crystal. Using the procedure in Ref. 8, we can obtain the following expressions for $\zeta^{\parallel}$ (**H**) and $\zeta^{\perp}$ (**H**):

$$\zeta^{\parallel}(\mathbf{H})=\frac{W_1^-A_1^-+W_2^-A_2^-}{W_1^+A_1^++W_2^+A_2^+},$$
$$\zeta^{\perp}(\mathbf{H})=\frac{W_1^{\sigma}(A_1^++A_1^-)+W_2^{\pi}(A_2^++A_2^-)}{2W^{\pi}(B^++B^-)}. \tag{3}$$

Here it is assumed that the recombination $[e(S_e^z)\leftrightarrow h(S_h^z)]$ of electrons and holes in DA pairs satisfies selection rules, just as in the case of free excitons. As a result, the transitions for the $\sigma^{\pm}$ and π polarizations are characterized by the following relative probabilities:

$$W_1^{\pm}(s_e^z=\pm 1/2\leftrightarrow s_h^z=\pm 1/2)=1/3,$$
$$W_2^{\pm}(\pm 1/2\leftrightarrow\pm 3/2)=1,$$
$$W_1^{\pi}(-1/2\leftrightarrow 1/2)=W_2^{\pi}(1/2\leftrightarrow -1/2)=W^{\pi}=2/3,$$
$$W_{1,2}^{\sigma}=W_{1,2}^{+}=W_{1,2}^{-}.$$

In addition, in the present work, as in Refs. 8, 11, and 12, it is assumed that the spin subsystem of the electrons and holes manages to undergo thermalization during the lifetime of a DA pair. Accordingly, the relative populations of the spin sublevels $E_D(\mathbf{H}, s_e^z)$ and $E_A(\mathbf{H}, s_h^z)$ are described by Boltzmann distribution functions, and $A_{1,2}^{\pm}$ and $B^{\pm}$ have the forms

$$A_1^{\pm}=\exp\left[\frac{\pm\Delta E_e(\mathbf{H})\mp\Delta E_h(\mathbf{H})}{2k_BT}\right],$$

$$A_2^{\pm}=\exp\left[\frac{(\pm\Delta E_e(\mathbf{H})\pm 3\Delta E_h(\mathbf{H})}{2k_BT}\right],$$

$$B^{+}=\exp\left[\frac{\Delta E_e(\mathbf{H})-\Delta E_h(\mathbf{H})}{2k_BT}\right],$$

$$B^{-}=\exp\left[\frac{-\Delta E_e(\mathbf{H})+\Delta E_h(\mathbf{H})}{2k_BT}\right].$$

Expressions (2) and (3) were used to approximate the functions $\zeta^{\parallel}(\mathbf{H})$ and $\zeta^{\perp}(\mathbf{H})$. The variable parameters used to find $\zeta^{\parallel}(\mathbf{H})$ and $\zeta^{\perp}(\mathbf{H})$ were P_e and P_h. The remaining parameters in Eqs. (2) and (3) were assumed to be known. They were characterized by the following values: $g_e=1.2$, $g_h=0.4$,[11] $I_e=0.2$ eV, $I_h=-0.4$ eV,[3] $x=0.008$. The values of $\langle s_{\mathrm{Mn}}\rangle_{H,T}$ at different field strengths were determined as described in Ref. 3. The best fit with experiment was obtained with the following values of the parameters: $P_e=0.75\pm0.03$ and $P_h=0.037\pm0.005$. (Theoretical curves *1* and *2* in Fig. 2 were constructed with these same values of the parameters.) According to the value of P_h, the exchange field acting on a hole in the A_0 state is much weaker than the field for a free exciton (reduction factor ≈ 25), and is somewhat weaker the field for an electron. Possible reasons for such drastic reduction of the exchange interaction of a spin s_h in the A_0 state with Mn^{2+} ions will be discussed below.

4. DISCUSSION

Let us consider possible reasons for the decrease in $G^*_{e(h)}$ and consequently in the large Zeeman splitting for bound impurity states. The Hamiltonian for the exchange interaction of carriers with the localized magnetic moments introduced by magnetic impurity atoms (Mn) may be represented in the form

$$\mathscr{H}^{\mathrm{int}}=\int d\mathbf{r}\sum_i I_{e(h)}(\mathbf{r}-\mathbf{R}_i)\rho_{e(h)}(\mathbf{r})\mathbf{s}_{e(h)}(\mathbf{r})\mathbf{s}_{\mathrm{Mn}}(\mathbf{R}_i), \tag{4}$$

where $\mathbf{s}_{e(h)}(\mathbf{r})$ and $\rho_{e(h)}(\mathbf{r})$ are the operators of the effective spin and density of states of the carrier at the point $\mathbf{r}$, $\mathbf{s}_{\mathrm{Mn}}(\mathbf{R}_i)$ is the operator of the spin of the magnetic field at the sites i occupied by impurities, and $I_{e(h)}(\mathbf{r}-\mathbf{R}_i)$ is the exchange interaction parameter. The simplest assumption which holds for states of large radius and disregards the magnetic polaron effect is that the quantum-statistical averaging can be performed independently for the magnetic Mn^{2+} ions, and $\mathbf{s}_{\mathrm{Mn}}$ can be replaced by its mean value in the magnetic field $\mathbf{H}$:

$$\langle s^z_{\mathrm{Mn}}\rangle=\beta_s\left(\frac{g_0\beta H}{kT}\right),\quad H_z=H_z, \tag{5}$$

where $\beta_s(y)$ is the Brillouin function and g_0 is the g factor of the magnetic field. The amplitudes of the splitting of the energy levels of the carrier (free or localized) are

$$\Delta E_{e(h)}=g_{e(h)}\beta H+I_{e(h)}\sum_i p_i^{e(h)}\langle S^z_{\mathrm{Mn}}\rangle,$$
$$I_{e(h)}=\frac{1}{v}\int I_{e(h)}(\mathbf{r}-\mathbf{R}_i)d\mathbf{r}, \tag{6}$$

where v is the volume per formula unit of ZnSe and $p_i^{e(h)}=v\rho_{e(h)}(\mathbf{R}_i)$ is the reduced (dimensionless) density of states of the carrier at site i.

When there are enough magnetic atoms in a volume with the radius of an impurity state r_0, configurational averaging with respect to the impurities may be performed in the last term in (6). Then $\Delta E_{e(h)}$ obeys expression (2), where

$$P_{e(h)}=\sum_l p_l^{e(h)}, \tag{7}$$

and the summation over l is carried out over all the lattice sites at which a magnetic ion may be found.

For the models of impurity sites usually employed (see, for example, Ref. 13), the value of $P_{e(h)}$ should be set equal to unity on the basis of the normalization conditions, despite the fact that a magnetic atom may not be found at the same site as the center that creates the electron (hole) impurity state of large radius. Then, as can be seen from (2), the magnitude of the large Zeeman splitting does not depend on the radius of the impurity state, and is the same as for a free carrier. This is due to the fact that any change in the radius of a state that results in a change in the number of magnetic ions interacting with it is compensated by a change in the density of states.

As we have already noted, the significant decrease in the large Zeeman splitting that we (as well as some other investigators[5]) observed for impurity acceptor levels can be attributed to different causes in the general case. For example, according to Ref. 4, the decrease in the large Zeeman splitting for weak solutions, in which $(v_0/v)x\ll 1$, where $v_0=\frac{4}{3}\pi r_0^3/3$, is attributable to the high probability that there are no magnetic ions in a volume v_0 with the radius of an impurity state r_0. However, the concentrations of such ions in the volume that we investigated are such that these conditions are not satisfied even for fairly deep impurity centers ($x=0.008$; $r_0=10$ Å; $v=0.45\times10^{-16}$ m^3; $4\pi r_0^3 x/3v\sim 1$).

Another reason for the decrease in the large Zeeman splitting for deep levels is realization of the magnetic polaron effect. In fact, the exchange interaction acting on most magnetic ions found within the volume of an impurity state is of order $(v/v_0)I_{e(h)}$, and may surpass the external magnetic field in modest fields, so that both expression (5) and the possibility of independent averaging with respect to the magnetic ions are unrealistic, i.e., expression (6) becomes invalid.[14] The magnetic polaron effect should also cause overall displacement of the impurity absorption lines by $xI_{e(h)}\langle s_{\mathrm{Mn}}\rangle$ (at very low temperatures). This shift is of the same magnitude as the maximum value of the splitting of the lines of free carriers in a magnetic field (i.e., $\Delta E_{e(h)}\approx 20$–$30$ meV for hole states). The magnetic polaron shift should vanish when $k_BT_m\approx(v/v_0)I_{e(h)}$, i.e., $T_m\approx 50$

K for the acceptor impurities in the $Zn_{1-x}Mn_xSe$ sample under consideration. However, neither displacement of the positions of the maxima of the photoluminescence lines nor a strong temperature dependence is, in fact, observed in the systems that we examined, suggesting that there is no magnetic polaron effect.

This contradiction can be explained by analyzing the model of an impurity center used and, in particular, the condition $P_{e(h)}=1$. As we have already noted, it can be confidently assumed that a magnetic atom cannot be found at the same site as a defect that initiates the appearance of the carrier impurity state under consideration. As a result, there should be restrictions on the summation over l in expression (7) for $P_{e(h)}$, which may cause a decrease in $P_{e(h)}$ and a resultant decrease in the large Zeeman splitting. Such arguments were advanced previously. However, in the widely adopted hydrogen-like model of a shallow state, the influence of the "crust" is usually small.[15] Then, as before, $P_{e(h)}$ should be close to unity and cannot be reduced in any way by an order of magnitude to account for the experimental data (Sec. 2), especially for acceptor impurities.

Impurity states caused by isovalent centers are often described with the aid of the one-parameter model of a center, which culminated in the work of I. M. Lifshits.[16] However, if this model is used to analyze the relatively shallow centers of large radius investigated in the present work (their binding energy is considerably smaller than the width of the forbidden gap of a carrier), no significant decrease in $P_{e(h)}$ can be achieved. This is due to the fact that in this model, too, the main part of the wave function of a center of large radius is distributed far from the defect.

We now turn to the model of a two-parameter impurity state, which was previously used to explain the character of electron and magnetic impurity states of large radius for various types of substances.[17] In particular, it was successfully used[18] to account for the advent of paired impurity levels located close to one another and to the edge of the spectrum that were observed in $ZnSe_{1-x}Te_x$.[19,20] In the one-parameter model, such states, which are due to impurities that are nearest or next-nearest neighbors, would be shifted relative to one another by an amount comparable to the width of the band from which they were split off.

The Hamiltonian of an impurity state in the model under consideration is

$$\mathscr{H}^{\text{imp}}=\sum_{\mathbf{k}}\varepsilon_{\mathbf{k}}a_{\mathbf{k}}^{+}a_{\mathbf{k}}+\varepsilon_1 a_0^{+}a_0+\frac{\gamma}{\sqrt{V}}\sum_{\mathbf{k}}(a_{\mathbf{k}}^{+}a_0+\varepsilon_{\text{b}}), \quad (8)$$

where ε_1 is the primary (atomic) energy of the impurity state, $\varepsilon_{\mathbf{k}}$ is the energy of band states of the matrix with wave vector $\mathbf{k}$, $a_{\mathbf{k}}^{+}$ and a_0^{+} are the creation operators of the respective states, γ is the hybridization parameter of the impurity and band states, and V is the volume of the crystal. Assuming that an impurity level is located near a band edge with a quadratic dispersion law $\varepsilon_{\mathbf{k}}=\hbar^2k^2/2m^*$, we obtain for the energy of an impurity level in the crystal

$$\varepsilon_0=\tilde{\varepsilon}_1\left[1-\frac{1}{2\delta}+\frac{\sqrt{1-4\delta}}{2\delta}\right], \quad \varepsilon_0,\ \tilde{\varepsilon}_1<0,$$

where

$$\tilde{\varepsilon}_1=\varepsilon_1-\frac{1}{V}\sum_{\mathbf{k}}(\gamma^2/\varepsilon_{\mathbf{k}}),$$

$$\delta=\tilde{\varepsilon}_1/\varepsilon_c, \quad \varepsilon_c=\gamma^4/E_1^3, \quad (9)$$

$$E_1=(4\pi)^{2/3}/2m^*v^{2/3}.$$

In (9), ε_c is the characteristic energy of the "subthreshold" region near the band edge.

The wave function of such a state (in the lattice-site representation) is

$$|\psi\rangle=\varphi_0(|a_0\rangle+\sum_{l\neq 0}\varphi_l|a_l\rangle),$$

$$\varphi_l=\frac{\gamma}{(4\pi)^{1/3}E_1}\frac{1}{r_l}\exp(-r_l/r_0), \quad (10)$$

$$r_0=\hbar/\sqrt{2m'|\varepsilon_0|},$$

where the subscript 0 refers to a site occupied by an impurity (a defect that leads to the appearance of an impurity level). The normalization factor φ_0 describes the probability $\mathscr{P}_0$ of finding a carrier at the zeroth site (i.e., at the impurity atom):

$$\mathscr{P}_0=|\varphi_0|^2=\left[1+\frac{1}{2}\frac{\varepsilon_c}{|\varepsilon_0|}\right]^{-1}. \quad (11)$$

For relatively deep levels beyond the subthreshold region ε_c (i.e., $|\varepsilon_0|\gg\varepsilon_c$, $|\delta|\gg 1$), $\varepsilon_0\approx\tilde{\varepsilon}_1$, and the main portion of the wave function is localized at the impurity site; only a small portion is smeared out over a region with the large radius r_0. Here the probability of finding a carrier away from the zeroth site equals

$$1-\mathscr{P}_0=\frac{1}{2}\frac{1}{\sqrt{\delta}}=\frac{1}{2}\sqrt{\frac{\varepsilon_c}{\varepsilon_0}}. \quad (12)$$

For shallow levels in the subthreshold region ε_c, for which $|\varepsilon_0|\ll\varepsilon_c$, $|\delta|\ll 1$, the main portion of the wave function is distributed over a broad region $4\pi r_0^3/3\gg v$, and only a small portion is found at the site occupied by the impurity atom, so that $\mathscr{P}_0\approx 2|\delta|\ll 1$.

Using (12) and assuming that the magnetic ions are distributed uniformly over all except the zeroth site, we obtain an expression for the energy of the Zeeman splitting of an impurity state in a magnetic field of type (2), where

$$P_{e(h)}=1-\mathscr{P}_0. \quad (13)$$

For shallow impurity levels, for which $|\delta|\ll 1$ and $P_{e(h)}\approx 1$, the magnitude of the splitting becomes close to the corresponding splitting for free states. The slight decrease in the large Zeeman splitting observed for the electron states of donor impurities and the drastic decrease in the large Zeeman splitting for the hole states in acceptors is readily attributable in the model under consideration to a decrease in $P_{e(h)}$, i.e., to the change in the character of an impurity state when the wave function is mostly localized at the impurity lattice site. An analysis of the change in

$P_{e(h)}$ from its value for free states does in fact make it possible to assess the character of the spatial distribution of the wave function of an impurity state.

It should also be pointed out that the exchange field acting on a magnetic ion from an impurity state of the type under consideration also decreases by a factor of $P_{e(h)}$ (i.e., it has a value of $\sim P_{e(h)}(\nu/\nu_0)I_{e(h)}$). Thus, the decrease in the large Zeeman splitting for the impurity center under consideration should be accompanied by corresponding reduction of the magnetic polaron effect. Just such behavior was observed in both our investigations and other experiments. Thus, this model makes it possible to eliminate the apparent inconsistencies when the entire body of experimental data on the Zeeman splitting of acceptor levels in a magnetic field is analyzed. This also confirms the suitability of our proposed model of an impurity center.

In conclusion, we note that similar measurements should be performed in the future on samples with other concentrations of magnetic impurity ions, which would make it possible to unambiguously interpret expression (1). We also note that the results can be used to analyze the magnetic polaron effect in different systems, as well as to explain the drastic decrease in the large Zeeman splitting for excitons localized on acceptors.

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