RAPID COMMUNICATIONS

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Direct measurement of exchange as a function of separation for discrete donor-acceptor pairs in ZnSe

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We describe optical detection of magnetic resonance for 17 well-resolved discrete zinc interstitial donor-zinc vacancy acceptor pairs of varying separation in ZnSe. For most of the pairs, microwave transitions are detected between the exchange split triplet and singlet manifolds giving a direct high-precision measurement of the separated electron and hole exchange interaction in the excited emitting state of each pair. From these studies the $E(+/2+)$ second donor state of the isolated interstitial zinc atom is estimated to be $\sim E_c - 0.8$ eV.

An important mechanism for luminescence in semiconductors is recombination between an electron trapped at one defect in the lattice (donor) and a hole trapped at another (acceptor).[1] Recently, in a study of distant shallow donor to acceptor luminescence in CdS, Cox and Davies[2] have demonstrated that exchange interactions between the separated electron and hole in the excited state can be revealed by optical detection of magnetic resonance (ODMR). In their study, discrete pairs were not resolved, either optically or in the magnetic resonance, but by combining ODMR with time- and wavelength-resolved spectroscopy they were able to deconvolute the broad ODMR spectrum to extract the general dependence of exchange on the pair separation.

In this Rapid Communication, we describe for the first time optical detection of magnetic resonance (ODMR) from $\sim$17 well-resolved *discrete* pairs of a single donor-acceptor system, which range in separation from nearest-neighbor distances to distances large enough that their exchange interaction is negligible. For most of the pairs, we detect sharp microwave transitions between the exchange split triplet and singlet states providing a direct high-precision measurement of the exchange interaction in the excited emitting state of each pair. We believe this represents the first such measurement of exchange by means of direct spectroscopic transitions between the triplet and singlet states of the excited state of any discrete luminescence system.[3]

The system studied is zinc selenide irradiated *in situ* at 4.2 K by 2.5 MeV electrons. The donor-acceptor pairs are Frenkel pairs composed of an interstitial zinc (donor) frozen into the lattice near the vacant lattice site (acceptor) from which it was displaced.[4] Because of this explosive "inside-out" method of production, we have a unique nonequilibrium distribution in which pairs of varying separation are on a somewhat equal footing. At the same time, the electron and hole turn out to be strongly bound to their respective defects ("deep"), their wave functions are highly localized, and the exchange interaction drops precipitously versus separation. We have, therefore, a textbook example of two exchange-coupled particles and we can probe for the first time their interactions over a wide range of discrete lattice separations.

The ODMR experiments were performed at 20 GHz in an EPR spectrometer fitted with 0.001-in. titanium windows for *in situ* irradiation at 4.2 K by 2.5 MeV electrons from the Lehigh University Van de Graaff accelerator. Optical excitation of $\sim$5 mW was provided from an argon-ion laser through an optical fiber terminating at a point in the microwave cavity just above the sample. The fiber was threaded through a concentric quartz capillary tube ($\frac{3}{16}$ in. diam$\times$48 in. long) which served in turn as a light pipe to guide the luminescence to an external silicon photodiode (EG&G 250 UV) or a cooled germanium detector (North Coast EO-817S).

The samples studied were single crystals grown by vapor transport in a sealed quartz ampoule. Both as-grown (high-resistivity) and zinc-fired (low-resistivity) n-type samples were studied. The samples were mounted so that irradiation could be performed with the e^--beam parallel to either the [111] or $[\bar{1}\bar{1}\bar{1}]$ direction. The spectral dependence of the ODMR was performed by inserting a $\frac{1}{4}$-meter Jarrell-Ash monochromator between the light-pipe and detector.

The ODMR spectrum observed by monitoring a broad luminescence band in the region 800–1100 nm is shown in Fig. 1. There is a strong central group of lines near 7 kG ($g\sim2$) labeled *A-D* and many additional sharp weaker lines which are spread over the full range of magnetic fields available. In a previous report,[4] we demonstrated that the central group arises from close Frenkel pairs for which the exchange interaction J is large enough that luminescence originates primarily from the total $S=1$ triplet state, the ODMR spectra reflecting in turn the allowed $\Delta M = \pm 1$ transitions within this manifold. The two strongest of these (A,B) were tentatively identified as arising from pairs for which the zinc interstitial is in the nearest stable[5] $\langle 111\rangle$ and $\langle 100\rangle$ positions from the vacancy. At that time the origin of the many other lines was not understood.

We now find that all of the lines (including *A-D*) can be explained as arising from several superposed spectra, but each described by the single common spin Hamiltonian

$$H_i = H_I + H_V + J_i \mathbf{S}_I \cdot \mathbf{S}_V + \mathbf{S}_I \cdot \tilde{D}_i \cdot \mathbf{S}_V \ , \qquad (1)$$

appropriate for zinc-vacancy–zinc-interstitial pairs of varying separations. Here H_I and H_V are the $s=\frac{1}{2}$ spin

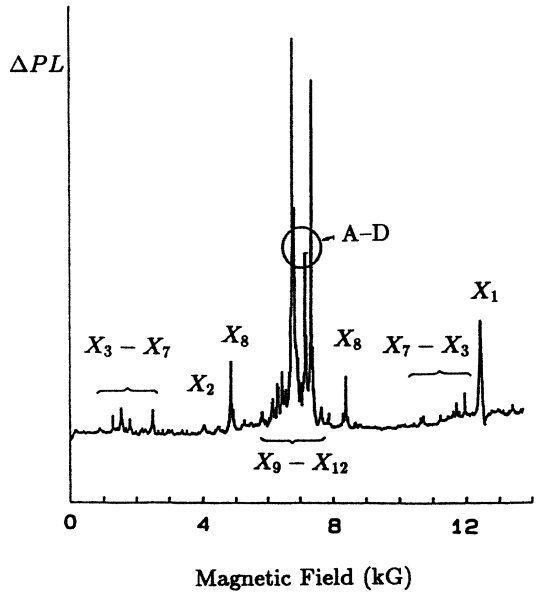

FIG. 1. ODMR spectrum detected from the total near-infrared luminescence in e^--irradiated ZnSe at 1.5 K with $\mathbf{B}\|[111]$ and $\nu = 20$ GHz.

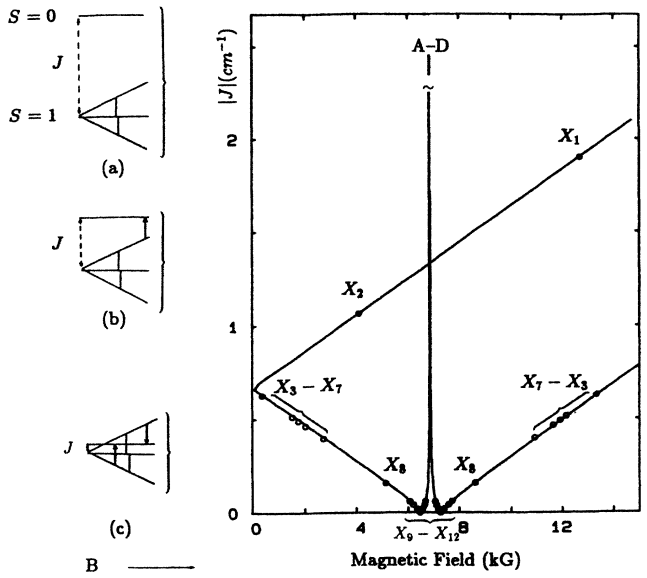

FIG. 2. Predicted magnetic field positions (solid lines) for the transitions of two exchange coupled particles vs $|J|$ for $g_I = 1.9664$, $(g_V)_\perp = 2.2085$, $\nu = 20$ GHz, and $\tilde{D}_i = 0$ in Eq. (1). The circled points are the experimental points for the indicated spectra. The insets (a)–(c) illustrate the schematic energy level schemes as a function of J.

Hamiltonians for the isolated Zn_I^+ interstitial[6] and the V_{Zn}^- vacancy,[7] respectively, the individual spectra differing only in the isotropic (J_i, exchange) and smaller traceless anisotropic ($\tilde{D}_i$, dipole-dipole) interactions between the two spins. We can conclude therefore that the recombination process is given by

$$Zn_I^+ + V_{Zn}^- \rightarrow Zn_I^{2+} + V_{Zn}^{2-} + h\nu \ , \qquad (2)$$

where the broad luminescence band contains contributions from pairs of many different separations.

The general features of the ODMR transitions that result from Eq. (1) are depicted in Fig. 2. Here we have plotted the predicted magnetic field positions for the transitions of Eq. (1) vs $|J|$ for $g_I = 1.9664$,[6] $(g_V)_\perp = 2.2085$,[7] $\nu = 20$ GHz, $\tilde{D}_i = 0$. (For $\mathbf{B}\|\langle 110\rangle$, this is the case for those orientations of each pair for which the vacancy $\langle 111\rangle$ dangling bond is perpendicular to $\mathbf{B}$. Inclusion of $\tilde{D}_i$ produces additional shifts, small on the scale of the figure but easily resolved in the spectrum.) For $|J| \gg g_{I,V}\mu_B B$, only $\Delta M = \pm 1$ transitions within the $S = 1$ manifold are observed, as depicted in inset (a). This is the case for spectra *A-D*. For smaller $|J|$, inset (b), an additional microwave transition between the $S = 1$ and $S = 0$ manifolds becomes possible. Although this $\Delta S = 1$ transition should be weak, it is detected easily by ODMR because it transfers the system from the triplet radiative "bottleneck" to the strongly radiative singlet state. A key identifying feature of this transition is that the resonance shifts to lower magnetic field if the microwave frequency is increased. This is observed for the transitions marked X_1 and X_2 in Fig. 1 and their positions are located accordingly in Fig. 2. When $|J| < g_{I,V}\mu_B B$, four transitions become possible for each pair, as shown in inset (c). Again the two transitions between the $S = 1$ and $S = 0$ manifolds tend to dominate because of the more radiative singlet state, but all four are observed for $X_9 - X_{12}$. Finally, with $|J| \ll (g_V - g_I)\mu_B B$, the lines converge to those of the isolated vacancy and interstitial.

Detailed analysis of the spectra and their angular dependencies reveals thirteen discrete resolved pairs (in addition to *A-D*) with J ranging from zero (isolated pairs) to -1.9 cm^{-1}. The results are summarized in Table I. The symmetry of each spectrum is indicated in the table along with the magnitude of the principal value of $\tilde{D}$. Included also is the temperature at which each pair spectrum disappears upon annealing (15 min isochronal) and the wavelength of the maximum photoluminescence associated with it.

Table I reveals several independent indicators of the separation r of the pairs: (1) The exchange interaction J and the dipole-dipole interaction $\tilde{D}$ should decrease with separation. (2) Because of the Coulomb interaction between Zn_I^{2+} and V_{Zn}^{2-} in the ground state, annealing should reflect annihilation and the annealing temperature should therefore increase with separation. (3) The photoluminescence energy is given by

$$E_{PL} \cong E_{Zn_I}(+/2+) - E_{V_{Zn}}(2-/-) + \frac{3e^2}{\varepsilon r} - E_{relax} \ , \qquad (3)$$

where the first two terms are the energy positions of the second donor and second acceptor states measured from the valence band for the isolated zinc interstitial and vacancy, respectively, the third term approximates the difference in the Coulomb energy between the excited $(Zn_I^+ + V_{Zn}^-)$ and the ground $(Zn_I^{2+} + V_{Zn}^{2-})$ states of the pair, and the last term is the energy change due to lattice

TABLE I. Experimental properties of the $Zn_I V_{Zn}$ Frenkel pairs in irradiated ZnSe. (J and D in units of 10^{-4} cm^{-1}, with uncertainty $\pm 0.2\%$ or $\pm 5\times10^{-4}$ cm^{-1}, whichever is the greater.) Question mark indicates unknown value.

	J	$\lvert D_i \rvert_{max}$	Symmetry	Anneal (K)	PL λ (nm)
A		98	C_{3V}	160	800
B		182	C_{1H}	180	800
C		~122[a]	C_{1H}	180	800
D		45	C_{3V}	200	860
X_1	−19030	750[a]	C_{1H}	180	800
X_2	−10690	?	?	180	?
X_3	−6280	?	?	200	~900
X_4	−5131	0	C_{3V}	200	~900
X_5	−4878	60	C_{3V}	200	~900
X_6	−4611	100	C_{3V}	200	~900
X_7	−3947	0	C_{3V}	200	930
X_8	−1585	100	C_{1H}	200	1000
X_9	−610	0	C_{3V}	200 to 260	~1000
X_{10}	−437	0	C_{3V}		~1000
X_{11}	−223	0	C_{3V}		~1000
X_{12}	−85	0	C_{3V}		~1000
V^-	~0	· · ·	C_{3V}	260	1100
Zn_I^+	~0	· · ·	T_D	260	1100

[a]Tentative.

relaxation differences in the ground and excited states. The Coulomb energy term decreases with r and the photoluminescence energy should therefore shift to longer wavelength. All of these indicators of separation in Table I are remarkably consistent.

With this information, plus the symmetry of the pair spectra, we are optimistic that we will eventually be able to identify each of the spectra with a specific pair configuration. This task is currently under study. In the meantime, however, we can point out a few tentative benchmark identifications which will help in this task. An important additional piece of information comes from monitoring the Frenkel pair alignment versus the bombarding electron-beam direction. This alignment can be measured directly from the relative intensities of the ODMR peaks associated with the differently oriented pairs in the lattice. The particular case of an interstitial located in a ⟨100⟩ direction from its vacancy reveals itself because a unique set of oriented pairs becomes equivalent. This is found to be the case for spectra B and X_8. These spectra are sufficiently intense to allow resolution of hyperfine structure associated with four equivalent ^{77}Se atoms surrounding the interstitial site. For these spectra, therefore, the interstitial is located in the normal stable[5] interstitial site surrounded by four selenium neighbors and displaced in a ⟨100⟩ direction. There are only a limited number of such sites at distances from the vacancy of 2.82 Å (the nearest site, assigned to the B spectrum), 8.48 Å, 14.10 Å, etc.

We tentatively assign X_8 therefore to the 14.10 Å separation because it is the nearest site that contains enough closer interstitial sites (16) to accommodate the large number of pairs listed in the table with greater exchange. Having made this assignment, we have already accounted for ~75% of the available sites inside this radius (11 out of 16).

With this assignment we can estimate the $E_{Zn_I}(+/2+)$ electrical level position using Eq. (3). The $E_{V_{Zn}}(2-/-)$ level has been measured to be $E_V+0.7$ eV.[8,9] We assume that the major contribution to the lattice relaxation energy comes from the Jahn-Teller relaxation of V_{Zn}^- measured to be ~0.4 eV.[8,9] With these and the Coulomb energy $3e^2/\varepsilon r = 0.35$ eV at $r = 14.1$ Å, the $E_{PL} = 1.24$ eV gives

$$E_{Zn_I}(+/2+) \cong E_V + 2.0\text{ eV} = E_c - 0.8\text{ eV}\ .$$

This is remarkably close to that for a He^+ ion ($Z=2$) in a uniform dielectric medium ($\varepsilon = 8.7$ for ZnSe, and using the free-electron mass appropriate for a deep state) of $E_c - 0.7$ eV, confirming the general consistency of the scale of lattice site identifications.

An overall picture of what we are learning is summarized in Fig. 3. The isolated interstitial zinc (+/2+) and isolated zinc vacancy (2−/−) levels are located at $\sim E_V+2.0$ and $E_V+0.7$ eV, respectively. From the distant shallow donor to vacancy recombination at 720 nm, the relaxation energy of the vacancy has been determined to be 0.4 eV.[8,9] Assuming that the vacancy relaxation is unaltered, the 625 nm distant shallow donor to V^I closest Frenkel pair luminescence[4] locates this closest pair level at $E_V+0.4$ eV. To these we can now sketch in the progression of ground and excited energy states for the neutral pair as the interstitial and vacancy approach each other. As shown, the $V_{Zn}(2-/-)$ level becomes the ground state and the $Zn_I(+/2+)$ level the excited state, the levels separating as the two components approach each other due to their Coulomb interactions.

It is interesting to note that for these deep donor and acceptor defects a substantial Coulomb interaction correction to the luminescence energy remains ($\sim \frac{1}{4}$ eV) even though the exchange interaction has decreased to zero.

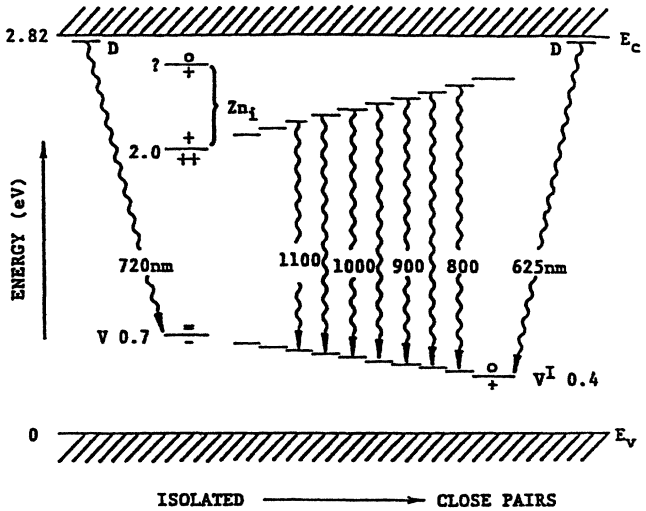

FIG. 3. Schematic diagram showing the energy-level positions and optical transitions for the isolated zinc vacancy, the isolated zinc interstitial, and the zinc Frenkel pairs.

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[3]N. R. J. Poolton, J. E. Nicholls, and J. J. Davies, J. Cryst. Growth (to be published), have estimated indirectly the exchange interaction for a complex defect in ZnSe involving Au by a second-order effect for ODMR transitions within the excited triplet manifold.

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[5]There are two available T_d interstitial sites in the ZnSe lattice, one surrounded by four nearest-neighbor Se atoms, the other by four Zn atoms. On a simple $Zn^{2+}Se^{2-}$ ionic model, the stable zinc interstitial site is that surrounded by four Se^{2-} ions.

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