Motional Enhancement of Exciton Magnetic Moments in Zinc-Blende Semiconductors

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We report a remarkable enhancement of the magnetic moments of excitons as a result of their motion. This surprising result, which we have observed in magneto-optical studies of three distinct zinc-blende semiconductors, GaAs, CdTe, and ZnSe, becomes significant as the kinetic energy of the exciton becomes comparable with its Rydberg energy and is attributed to motionally induced changes in the internal structure of the exciton. The enhancement of the magnetic moment as a function of the exciton translational wave vector can be represented by a universal equation.

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The concept of an exciton is key to the understanding of the opto-electronic properties of many materials. In semiconductors, excitons are of the Wannier type, in which an electron is bound to a hole by the Coulomb interaction, so that the resulting states are the analogues of those in a hydrogen atom. This classic model, in which the ground state is taken to be of hydrogenic $1S$ form, is used not only in introductory texts but also in more advanced treatments and has proved very successful in describing the energy levels of excitons at rest. In contrast, the behavior of excitons when they are moving is not well understood and the question arises of whether the hydrogenic model has to be significantly modified when excitons acquire kinetic energy. The experiments described in this Letter show that such a modification is indeed required and provide evidence that the internal structure of excitons becomes significantly changed as a result of their translational motion. In other words, unlike the case of a hydrogen atom in free space, we find that the wave function describing the relative motion of the particles which make up the exciton changes as the exciton moves. An understanding of these motional effects is of both fundamental and applied importance since excitons provide a major source of energy transport through crystal structures and in many opto-electronic devices.

Our work is based on measurement of the magnetic moment of the exciton as a function of its kinetic energy. The magnetic moment is extremely sensitive to the form of the exciton's wave function and, remarkably, we find that it increases hugely, in some cases by a factor approaching ten, as the exciton acquires kinetic energy. We have observed this new phenomenon in three distinct materials (CdTe, ZnSe, and GaAs) and believe it to be a universal property of excitons in zinc-blende semiconductors. In contrast to a hydrogen atom moving in free space, the exciton moves through a medium (the crystal) which interacts strongly with the electron and hole. The interaction gives rise to coupling between the excitons's translational motion and the relative motion of the particles within it and this changes the nature of the ground state wave function. The enhancement is thus a direct manifestation of motionally induced changes in the exciton's internal structure.

The magnetic moments of the excitons can be determined by applying a magnetic field and measuring the Zeeman splittings that occur in the excitonic transitions. By confining the excitons in quantum wells (QWs), we can study excitons of specific translational wave vectors and therefore of specific kinetic energy. The essential feature of our work is the use of wells that are sufficiently wide (relative to the exciton Bohr radius) for the two-particle motion to be considered within the "adiabatic" approximation (see, e.g., Refs. [1–3]), in which the exciton is treated as a composite particle formed by the electron and hole mutually orbiting each other (the internal motion) plus a translational motion of their center of mass. If the excitons are confined in QWs that are sufficiently deep (compared with the exciton binding and confinement energies), the infinite well approximation can be used. The

exciton center of mass wave function is set to zero at the boundaries and the component K_z of the exciton wave vector perpendicular to the plane of the well (i.e., in the growth direction, taken to be the z axis) is quantized according to $K_z = N\pi/L$, where N is a nonzero integer and L is the well width (see, e.g., Ref. [4]). By applying a magnetic field in the z direction we have studied the Zeeman splittings of the optical transitions that correspond to each individual quantized exciton state (in some cases with values of N approaching 30). For (001) QWs we find that the splitting (characterized by an effective g value g_{exc}) is, for all materials, a strong function of N, and thus of K_z. In other words, the excitons's magnetic moment is highly dependent on its kinetic energy.

Our specimens were grown by molecular beam epitaxy. Those with (001) QWs were of three types: (i) CdTe wells with widths ranging between 66 and 177 nm, with either $Cd_{0.92}Zn_{0.08}Te$ or $Cd_{0.94}Mn_{0.06}Te$ barriers [5]; these layers were grown pseudomorphically on $Cd_{1-x}Zn_xTe$ substrates for which $x = 0.04$ or $x = 0.11$; the CdTe wells are therefore strained because of the different lattice constants of CdTe and $Cd_{1-x}Zn_xTe$, leading, at $K_z = 0$, to the heavy-hole (HH) states being at about 12 meV (for $x = 0.04$) or 33 meV (for $x = 0.11$) lower than those of the light-hole (LH); (ii) an (unstrained) GaAs well of width 240 nm with 400 nm $Al_{0.3}Ga_{0.7}As$ barriers, grown on a 100 nm GaAs buffer layer on a semi-insulating GaAs substrate; (iii) a ZnSe well of width 50 nm with ZnSSe barriers, grown strained on a GaAs substrate, so that here the heavy-hole states at zero wave vector lie 13 meV beneath those of the light holes. A further CdTe QW (width 66 nm, $Cd_{0.92}Zn_{0.08}Te$ barriers) was grown on a (110) $Cd_{0.97}Zn_{0.03}Te$ substrate.

Figure 1(a) shows the zero-field reflectivity spectrum taken from the 240 nm GaAs quantum well at 10 K. A well-resolved series of resonances is visible to the high energy side of the bulk GaAs exciton resonance energy of $E_0 = 1.514$ eV. For an exciton translational mass $M_{\mathrm{HH}} = m_e^* + m_{\mathrm{HH}}^*$ (where m_e^* and m_{HH}^* are, respectively, the electron and HH effective masses), the transition energies are given by $E_0 + N^2h^2/8M_{\mathrm{HH}}L^2$ and the excellent fit to the data in Fig. 1(b) shows the infinite well approximation to be valid. Strictly, we should consider the coupled exciton-photon (polariton) system (as in Refs. [4,6]); however, the polariton dispersion curves for the GaAs specimen [Fig. 1(b)] show that the present measurements are for values of K_z sufficiently large for the simple uncoupled excitonic approximation to be appropriate. The relative strength of the reflectivity features for odd and even N depends [4] on L/λ, where λ is the wavelength of the light in the material and, for the GaAs well, we observe only the odd values.

It is when a magnetic field B is applied in the [001] direction (the z axis) that the unusual behavior is observed. The differences in energy between the exciton resonances in σ_+ and σ_- circular polarizations were measured by reflectivity or by photoluminescence excitation (PLE) spectroscopy with light incident along the z axis, so that the excitons created have zero in-plane momentum. Our experiments concern the HH exciton, which involves an electron and a heavy hole, with spin and angular momentum projections of $m_s = \pm 1/2$ and $m_J = \pm 3/2$, respectively. Light of polarization $\sigma_\pm$ creates HH excitons with angular momentum ± 1, corresponding to the states $|m_J = \pm 3/2, m_s = \mp 1/2\rangle$. When the field is applied, these transitions are split in energy by an amount $g_{\mathrm{exc}}\mu_B B$, where μ_B is the Bohr magneton. If the electron and hole behaved independently, we would have $g_{\mathrm{exc}} = (g_e - g_{hh})$, where g_e and g_{hh} are, respectively, the electron and heavy-hole g values [7] for the field along [001]. We

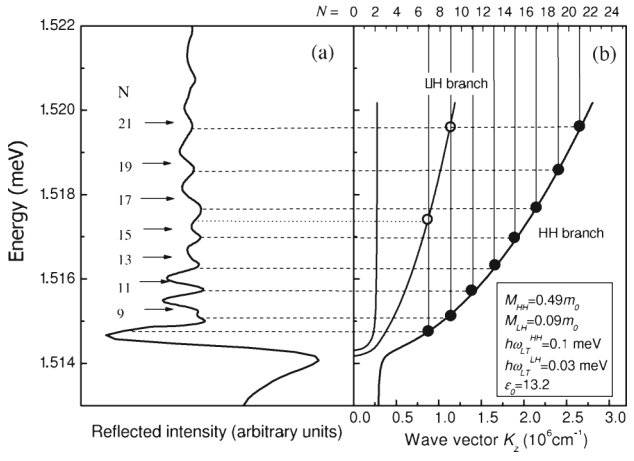

FIG. 1. Left: the reflectivity spectrum from a 240 nm GaAs quantum well at 10 K and zero magnetic field. Right: the positions of the reflectivity signals on the excitonic polariton dispersion diagram. The translational quantization index N appears at the top of the diagram. Open and closed circles denote light-hole and heavy-hole excitons, respectively.

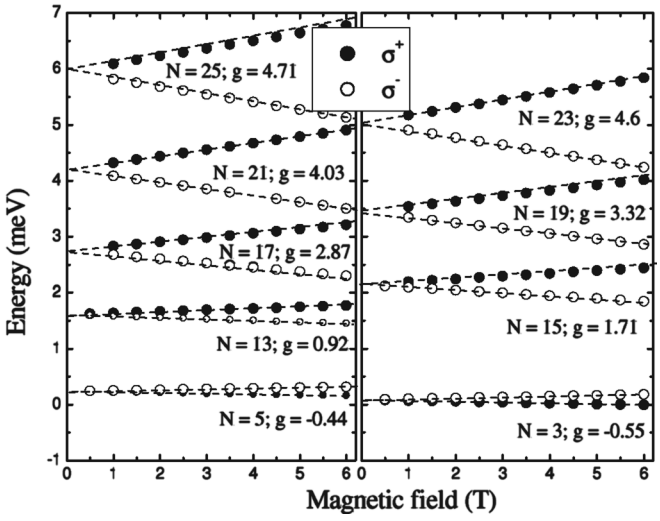

FIG. 2. Magnetic field dependences of the σ_+ and σ_- energies for the 240 nm GaAs quantum well reflectivity signals for various values of N. Data for $N = 3, 17\ldots$ are offset from those for $N = 5, 13\ldots$ for clarity.

would not expect g_{exc} to depend on the quantization index N. The data for the GaAs well (Fig. 2) *show clearly that this prediction is not fulfilled*. The splitting is accurately linear in B, but there is a very marked increase as the quantization index increases, corresponding, for the largest values of N, to values of g_{exc} of more than 5. For GaAs, we also observe features related to quantized LH excitons, but they are too weak for their Zeeman splittings to be measured.

For CdTe QWs, the data are equally remarkable. We first describe the data for wells of three different widths grown on $Cd_{0.96}Zn_{0.04}Te$ substrates. Typical PLE spectra in a magnetic field are shown in Fig. 3(a). We again observe a strong dependence of g_{exc} on the quantization index N. Furthermore, we find that, if the g factors for CdTe for all three well widths are plotted against $K_z = \pi N/L$ *they lie on a common curve*, showing that it is K_z, rather than N, that is the controlling parameter.

Similar behavior is observed for the more highly strained CdTe QWs, though the Zeeman splittings at a given K_z are smaller than those for wells on $Cd_{0.96}Zn_{0.04}Te$. Furthermore, in the ZnSe case, we again see a strong dependence of g_{exc} on K_z.

Figure 4 shows a further remarkable feature of the g factors, in that, irrespective of the material, they can be represented for all specimens by an equation of the form

$$g_{exc} - g_0 \approx \frac{1}{2} G\left(1 - \frac{1}{\sqrt{1 + \alpha^2 (a_{exc} K_z)^4}}\right), \qquad (1)$$

where G and α are dimensionless constants and a_{exc} is the exciton Bohr radius (introduced to make the term involving K_z dimensionless). From experiment, g_0, the value of g_{exc} at $K_z = 0$, is quite small (-0.55 for GaAs, 0 for CdTe and -0.40 for ZnSe). We take a_{exc} to be 14.5, 6.9, and 4.1 nm for GaAs, CdTe, and ZnSe, respectively [8,9]. The form of Eq. (1) is justified later in the Letter. To fit the four cases (GaAs, CdTe on $Cd_{0.96}Zn_{0.04}Te$, CdTe on $Cd_{0.89}Zn_{0.11}Te$, and ZnSe) we have used values of α of 0.12, 0.48, 0.17, and 1.0, respectively, with $G = 16.5$ (GaAs), 14.5 (CdTe), and 12.5 (ZnSe). The observation of the enhancement in both strained and unstrained (001) wells shows that it is not a direct consequence of the strain, though the difference between the CdTe data for the two types of $Cd_{1-x}Zn_xTe$ substrate indicates that the degree of strain is relevant.

A further key observation is that, for the (strained) CdTe (110) quantum well, the Zeeman splitting does *not* depend on K, its magnitude being constant with $g_{exc} = 1.3$ for all observed values of N [see Fig. 3(b)].

We now seek a source for the large contributions to g_{exc} at high values of K_z. From Fig. 4 we see that the enhancement occurs when $K_z a_{exc} \alpha^{1/2}$ is of order unity, that is (since $\alpha^{1/2}$ is itself of order unity) when the translational wavelength of the exciton becomes comparable with or smaller than the exciton Bohr radius or, equivalently, when the translational kinetic energy becomes comparable with the exciton Rydberg energy. This suggests that the behavior is associated with the onset of failure of the approximations which led to the $1S$ hydrogenic ground state. We therefore assume that, at large K_z, the $1S$ state is mixed with higher energy hydrogenic states with nonzero orbital angular momentum. The g values of these states will be large (since the effective Bohr magneton will be scaled by the inverse of the exciton reduced mass, of order 0.1).

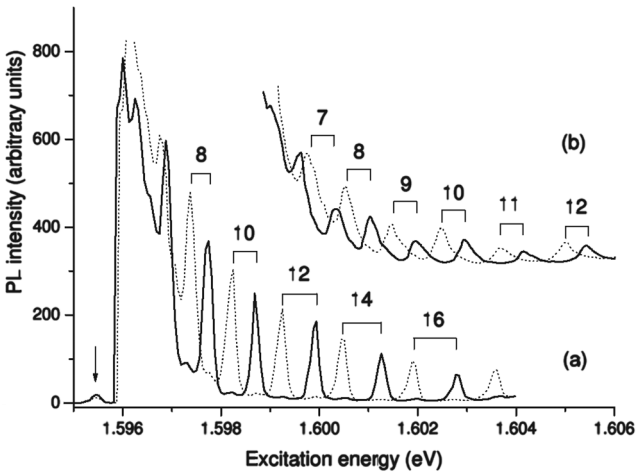

FIG. 3. (a) The σ_+ (solid lines) and σ_- (broken lines) PLE spectra at 3 K from a 144.2 nm CdTe (001) QW on $Cd_{0.96}Zn_{0.04}Te$ in a magnetic field of 4.0 T. The increase of Zeeman splitting with quantization index N is apparent. The arrow indicates the detection energy. For energies below 1.5959 eV, an attenuator was inserted. (b) Corresponding data at 6.5 T for the 66 nm (110) CdTe QW.

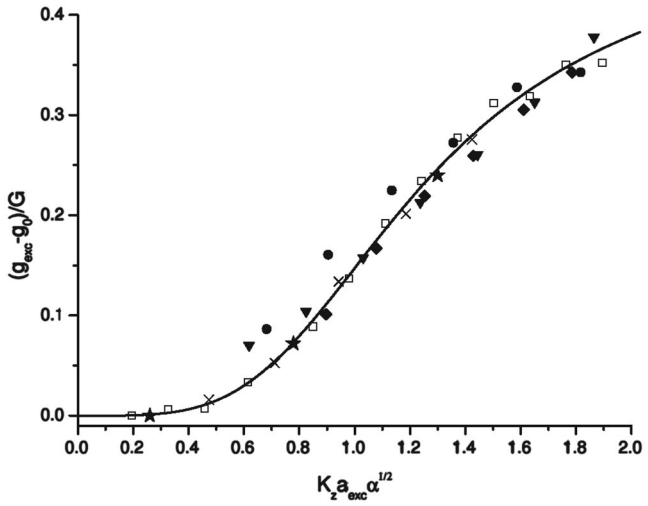

FIG. 4. The exciton g values for (001) QWs (relative to their values at $K_z = 0$) and normalized to the quantity G as a function of $K_Z a_{exc} \alpha^{1/2}$. Open squares denote the GaAs well, closed symbols denote the CdTe wells on $Cd_{0.96}Zn_{0.04}Te$ (the circles, triangles, and diamonds represent quantum wells of widths 66.0, 144.2, and 167.1 nm, respectively); crosses represent the CdTe wells on $Cd_{0.89}Zn_{0.11}Te$ and stars represent the ZnSe well. The curve is from Eq. (1).

To predict the form of the variation in g_{exc} we use a very simple model in which we consider explicitly only the mixing between $1S$ HH and $2P$ HH states. At low values of K_z, the experiments show that $(g_{\mathrm{exc}} - g_0)$ is proportional to K_z^4, suggesting that the operator responsible should have an off-diagonal matrix element of the form qK_z^2, where q is to be determined. The fraction of $2P$ character in the ground state is now $\sin^2\theta$, where $\tan 2\theta = 2qK_z^2/E$, E being the energy difference between the $1S$ and $2P$ states (3/4 of the exciton Rydberg). At finite K_Z the mixing leads to an additional contribution $(g_{\mathrm{exc}} - g_o)$ to the exciton g value of $g_{2P}\sin^2\theta$, where g_{2P} is the g value of the state that is mixed in. Writing $q = \alpha a_{\mathrm{ex}}^2/2E$ then leads to Eq. (1), with $G = g_{2P}$.

If the $2P$ states mixed in to the $1S$ states with $m_J = \pm 3/2$ have components of orbital angular momentum $m_l = \mp 1$, we expect g_{2P} to be $2/\mu$, where μ is the HH exciton reduced mass (in units of the electron rest mass) and thus to be of order 17 (ZnSe), 25 (CdTe), and 50 (GaAs) for the materials considered here. The values found for G (12.5, 14.5, 16.5) from the fits in Fig. 4 are somewhat smaller than these, but given the extreme simplicity of the approximation (in which we consider mixing only with the $2P$ state), this order of magnitude agreement is reasonable.

To identify the origin of the mixing, we consider the basic Luttinger Hamiltonian [10], which accounts for the energies of electrons and holes in zinc-blende materials in terms of their k vectors. Additional higher order terms derived from the theory of invariants are described in Refs. [1,2,11]. The Hamiltonian can be extended to the case of excitons by expressing it in terms of the coordinates of the relative (internal) and translational motion (see, e.g., Refs. [1–3]). The hole momentum $\hbar\vec{k}_h$ can then be written as $(-\vec{p} + \beta\hbar\vec{K})$, where $\beta = m_{\mathrm{HH}}^*/(m_{\mathrm{HH}}^* + m_e^*)$. Here $\vec{p}$ represent the momentum of the hole within the exciton while $\vec{K}$ represents the translational motion. Substituting in this way leads to several terms which, for finite exciton wave vector $\vec{K}$, can mix the $1S$ ground state with higher lying states. The reason for this is that these terms contain K_z^2 coupled with the internal momentum operator $\vec{p}$, which can mix $1S$ with nP states.

The mixing operator has not only to contain K_z^2 but must also vanish for (110) quantum wells. The only term in the Hamiltonian that satisfies these conditions is the term $\delta H = a_2\gamma_v\sum_i J_i^3\kappa_i$, where $a_2\gamma_v$ is a constant, $\kappa_i = k_i(k_{i+1}^2 - k_{i-1}^2)$ and i refers in turn to each of the x, y, and z directions [1,2]. This term contains components of the form $-a_2\gamma_v K_z^2[J_-^3 p_+ + J_+^3 p_-]/8\hbar$, where $p_\pm = p_x \pm ip_y$, which, for (001) quantum wells, can mix the $1S$ $(m_J = \pm 3/2)$ and nP $(m_l = \mp 1)$ HH states. To account for our data, the values required for $a_2\gamma_v$ are 2.1, 2.0, 0.7, and 1.8 eV nm^3 for GaAs, CdTe on $Cd_{0.96}Zn_{0.04}Te$, CdTe on $Cd_{0.89}Zn_{0.11}Te$, and ZnSe, respectively, (there are no reliable measurements of these parameters from other sources and the CdTe results suggest that they may be strain dependent). For (110) wells, explicit calculation shows that the mixing into the exciton ground state by δH does not contribute to the magnetic moment, in accord with the observations for CdTe. The calculation is clearly oversimplified, since the infinity of other nP HH states (and states of even higher angular momentum) can be mixed in and it is also possible that mixing with LH states is in reality important, since this could also introduce a strain dependence. The simple model does nevertheless provide considerable insight into the observed behavior.

To summarize, we have observed a remarkable change in the magnetic moment of excitons in (001) quantum wells as their K vector increases. We have considered a mechanism which involves motionally induced mixing of nP states into the $1S$ hydrogenic state. This mixing is significant, since the change in g value is large. In other words, the increase in the K vector is accompanied by a significant change in the internal structure of the exciton. The experiments suggest strongly that the effect is universal for zinc-blende structures and should therefore be taken into account in a wide variety of experiments that concern excitons in semiconductors. As an example, the results show clearly that the g value of an exciton is not always simply the sum of the individual values for the electron and hole, as has sometimes been assumed.

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