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Electron g-factor for cubic $Zn_{1-x}Cd_xSe$ determined by spin-flip Raman scattering

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We present spin-flip Raman-scattering measurements of the g-factor for electrons bound at neutral donors in cubic $Zn_{1-x}Cd_xSe$ $(0 \leqslant x \leqslant 1)$ grown by molecular-beam epitaxy. Excitation in resonance with the donor-bound exciton luminescence transition in the presence of a magnetic field produces Raman signals associated with transitions between the spin states of the bound electron. The dependence of the Raman shift of the signals on the magnetic field allows an accurate determination of the electron g-factor. For the particular case of cubic CdSe, the g-factor was measured to be $+0.42 \pm 0.01$. Five-band $\mathbf{k} \cdot \mathbf{p}$ perturbation theory was successfully used to reproduce the experimental dependence of the g-factor on Cd content, which can be approximated well by $g(x) = 1.16 - 0.56x - 0.18x^2$.

I. INTRODUCTION

The electron gyromagnetic ratio (g-factor) describes the magnitude of the Zeeman splitting between the two spin states of an electron in a magnetic field. In semiconductors, its value can differ substantially from the value $g_0 \approx 2$ for a free electron in vacuum and can be positive or negative. For conduction electrons and electrons bound in conduction-band related states (shallow donors, excitons), the g-factor is, like the effective mass, very sensitive to the band structure of the material. The determination of g can therefore be used to test band-structure theories. The g-factor is also affected by quantum confinement and its measurement can improve the understanding of low-dimensional semiconductor structures. The experimental methods used for this purpose include a variety of spin resonance and magneto-optical techniques. Among the latter, spin-flip Raman scattering (SFRS) has proved to be one of the most powerful, especially in the context of epitaxial layers. Since the original prediction of electron spin-flip Raman processes in semiconductors,[1] SFRS has been successfully applied for the investigation of g-factors both in bulk semiconductors and in low-dimensional structures. Reviews of SFRS are given in Refs. 2–4.

In the present work, SFRS is applied to epitaxial cubic $Zn_{1-x}Cd_xSe$ $(0 \leqslant x \leqslant 1)$ to investigate changes of the electron g-factor with Cd content. It is well established that, in the bulk, crystals of $Zn_{1-x}Cd_xSe$ have a cubic (zinc-blende) structure for $x \leqslant 0.3$, a hexagonal (wurtzite) structure for $x \geqslant 0.5$, and mixed phases for $0.3 \leqslant x \leqslant 0.5$.[5] In contrast, as shown recently, the growth of $Zn_{1-x}Cd_xSe$ alloys on zinc-blende substrates by molecular-beam epitaxy (MBE) can result in single-phase cubic crystalline layers over the entire composition range from ZnSe to CdSe.[6–8] The present work was carried out because the g-factors provide insight into the band structure of the cubic form of this ternary material. Furthermore, knowledge of the g-factors of the ternary compound is a necessary prerequisite for the understanding of the magnetic behavior of electrons in $Zn_{1-x}Cd_xSe/ZnSe$ quantum-well structures and in CdSe/ZnSe quantum-dot systems.

II. EXPERIMENT

The samples of cubic $Zn_{1-x}Cd_xSe$ were grown by MBE on substrates of (100) GaAs ($x = 0.04$, 0.15, 0.24, 0.42, 0.61; Heriot-Watt University) or on (100) InAs ($x = 1$, cubic CdSe; Ioffe Institute). The choice of InAs instead of GaAs for the growth of cubic CdSe reduces the density of extended defects that would otherwise be caused by the large CdSe/GaAs lattice mismatch. The Cd content determination was based on low-temperature measurements of excitonic photoluminescence (PL) and reflectance and is in a good agreement with the growth calibrations[9] based on reflection high-energy electron-diffraction (RHEED) oscillations. The thicknesses of the epilayers (around 1 μm) and confirmation that they were of the fully relaxed cubic modification were obtained by RHEED and x-ray-scattering measurements.

The SFRS experiments were carried out in magnetic fields up to 14 T in the Voigt and Faraday backscattering geometries. The samples were kept in an optical exchange-gas cryostat at a temperature of about 4 K. Tunable dye and titanium sapphire lasers pumped by an Ar^+-ion laser were used for SFRS excitation. Linearly polarized light was used for the SFRS excitation and signal detection, the incident power being kept below 0.1 W/cm^2 to avoid heating of the

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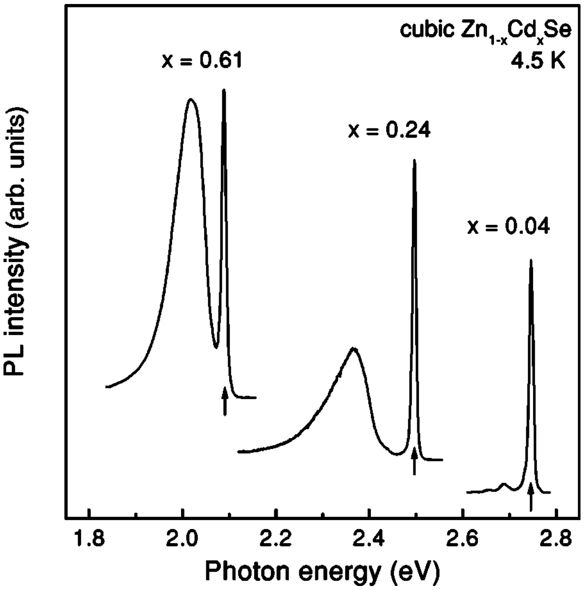

FIG. 1. PL spectra of cubic $Zn_{1-x}Cd_xSe$ with different Cd content, x. The arrows indicate the SFRS excitation energies. The spectra for $x=0.24$ and 0.61 were shifted along the y axis for clarity. $T=4.5$ K.

sample. The scattered light was analyzed by a SPEX 1404 double monochromator equipped with a cooled photomultiplier and a conventional single-photon counting system.

III. RESULTS

A. PL spectra

Figure 1 shows the PL spectra of cubic $Zn_{1-x}Cd_xSe$ alloys with three different values of the Cd content. The spectra demonstrate two main PL features commonly observed in epilayers of $Zn_{1-x}Cd_xSe$ grown on GaAs. The broad emission on the low-energy side of each of the spectra arises from defects that have not yet been identified. The strong and relatively narrow band (width 8–10 meV) on the high-energy side was attributed in Ref. 7 to PL of an impurity bound exciton. Our spectra are consistent with this interpretation, since the higher-energy PL band lies about 5 meV beneath the free-exciton feature in the reflectance spectra, a typical binding energy of an exciton to a shallow donor. This assignment also agrees with other work on $Zn_{1-x}Cd_xSe$ in which, despite experimental indications of exciton localization by compositional fluctuations, the near-edge PL is dominated by the emission of *bound* excitons.[10] Since ZnSe and CdSe are normally n-type, we assign the higher-energy PL band to the recombination of excitons bound at neutral donors (D^0X). The shift of this band and of the free-exciton feature in the reflectance spectra to lower energy with increasing Cd content reflects the reduction of the alloy band gap and is in good agreement with calculations.[11] The transition with a peak at 1.745 eV in the PL spectrum of the pure CdSe sample (Fig. 2) is also attributed to D^0X.[12]

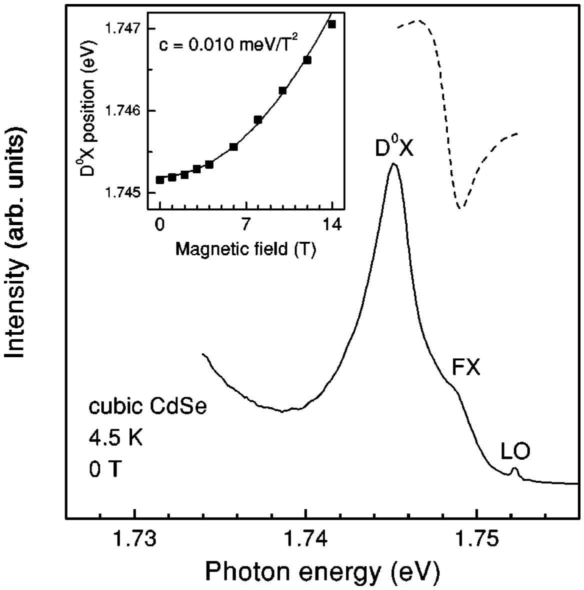

FIG. 2. PL (solid) and reflectance (dashed) spectra of cubic CdSe taken at $T=4.5$ K and $B=0$ T. The labels FX and D^0X indicate the free exciton and neutral donor bound excitonic PL bands, respectively. LO marks the LO-phonon Raman signal. The inset presents the diamagnetic shift of the PL peak for the D^0X band.

B. SFRS spectra

Spin-flip Raman scattering consists of the inelastic scattering of light from a charge carrier in a semiconductor when, in the scattering process, the spin state of the charge carrier is altered. When the semiconductor is placed in a magnetic field B, the two electron-related spin states $m_s=\pm\frac{1}{2}$ split in energy by an amount

$$\Delta E=g\mu_B B, \tag{1}$$

where g is the absolute value of the electron g-factor and μ_B is the Bohr magneton. The shift in energy between the incident (ω_i) and scattered (ω_s) light (Raman shift) is a direct measure of this splitting, $\hbar(\omega_s-\omega_i)=\Delta E$, so that g is readily determined. The g-factors of conduction-band electrons, electrons in excitons, electrons in excitons bound to shallow impurities, and electrons bound to donors are expected to be the same.[13]

The SFRS experiments presented in this paper were performed by exciting in resonance with the PL transitions identified above as being D^0X. The advantage of such resonance excitation lies in the fact that the exciton forms the intermediate state in the scattering process and a strong enhancement of an electron spin-flip signal is expected when the incident photon energy $\hbar\omega_i$ approaches the energy of the excitonic state. Such resonant enhancement has been used widely for the investigation of SFRS in semiconductors (see, for example, Refs. 13 and 14).

In Fig. 3, we show SFRS spectra for cubic CdSe obtained when the excitation is tuned to the energy of D^0X. In the Voigt geometry (the direction of B is perpendicular to the sample growth direction Z), strong Stokes and anti-Stokes Raman signals are detected when the linear polarizer and analyzer are crossed. In contrast, these signals are very weak in the Faraday geometry ($B\|Z$), independent of the polarization conditions. This behavior corresponds to the selection rules for an electron spin-flip. We note that the Stokes and anti-Stokes signals satisfy different resonance conditions[13]

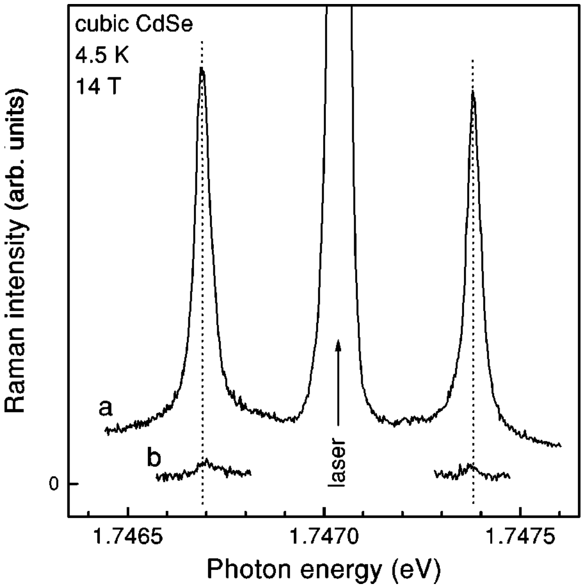

FIG. 3. SFRS spectrum of the donor electrons in cubic CdSe taken in (a) backscattering Voigt and (b) Faraday geometries. $T=4.5$ K, $B=14$ T. For clarity, the laser line in case (b) is not shown. The dashed lines are guides for the eye.

and their intensities in Fig. 3 are in general not in the ratio of a Boltzmann factor as a result. The Raman shifts of the Stokes and anti-Stokes signals are equal for both geometries and vary linearly with the magnetic field (Fig. 4). By use of Eq. (1), we obtain for cubic CdSe $g=0.42\pm0.01$ (note that the linear fits pass through the origin within experimental error). We observe also that the g-factor is isotropic, as expected for the SFRS of states related to the conduction band (i.e., free or shallow donor-bound electrons) in the cubic modification of the sample under study. Any anisotropy would suggest, for example, the existence of the wurtzite CdSe phase, or of a large strain in the cubic CdSe layer, or that the signals observed originate from scattering between valence-band–related states.

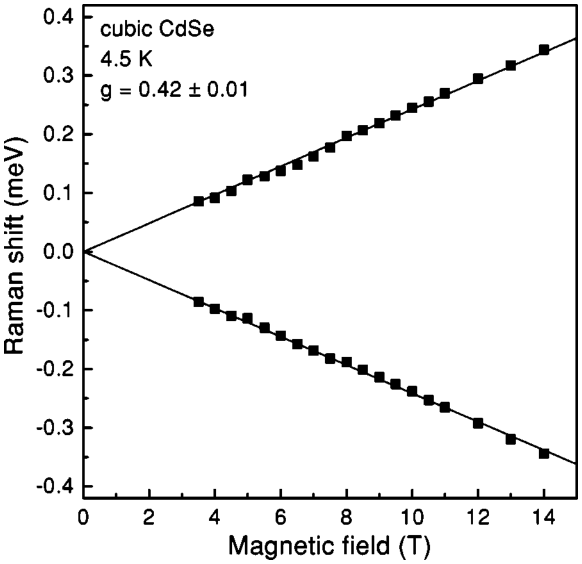

FIG. 4. Magnetic-field dependence of the Raman shift for the Stokes signals (positive shifts) and anti-Stokes signals (negative shifts) of CdSe shown in Fig. 3.

The existence of a diamagnetic shift with the quadratic coefficient $c=0.010\pm0.001$ meV/T^2 for the $D\,^0X$ PL band (see inset, Fig. 4) leads to the situation in which the excitation energy (kept constant in our experiments) passes through a large part of the PL band (width ~3.5 meV) when B changes from 14 T to 3.5 T (at lower values of B, the signals are not spectrally resolved). This affects both the absolute and relative intensity of the Stokes and anti-Stokes signals because of changing resonance conditions (for details, see Ref. 13) but does not affect the observed Raman shifts or the value of the g-factor that we obtain.

Qualitatively similar SFRS spectra were measured for the $Zn_{1-x}Cd_xSe$ samples with different Cd contents. Strong Stokes and anti-Stokes signals demonstrate the same selection rules as for cubic CdSe and, again, there is a linear dependence of the Raman shifts on the magnetic field. As before, the SFRS signals were obtained in resonance with $D\,^0X$ and are attributed to the donor-bound electron spin flip; when exciting at different points of the $D\,^0X$ PL, we do not observe any variation in the g-factor within experimental error.

These observations contrast to other studies of ours on epitaxial fractional CdSe monolayers in ZnSe barriers,[15] where we observe SFRS transitions between the spin-split levels of localized excitons, rather than between the levels of a donor-bound electron; in the former case, Eq. (1) no longer describes the dependence on a magnetic field of the SFRS shifts, due to a finite zero-field splitting arising from the electron-hole exchange energy, while the parameters of the exciton spin Hamiltonian also show a significant dependence on excitation energy due to the effects of varying degrees of localization in that highly inhomogeneous system. In view of the relative simplicity of the present observations, we therefore rule out SFRS between excitonic levels as an explanation of the present data.

IV. DISCUSSION

Figure 5 presents the g-factors measured for the samples with different x. It includes also the value of $g=1.15\pm0.01$ for epitaxial ZnSe on (100) GaAs, which we measured also by SFRS as part of this work. This value is close to the value of $g=1.120\pm0.001$ for electrons in conduction-band-related states determined by an optically detected magnetic resonance (ODMR) experiment.[16] Direct measurements using circularly polarized microwave radiation in this ODMR experiment established also that the ZnSe g-factor is positive.[17] This value of g also agrees well with that calculated via five-band $\mathbf{k}\cdot\mathbf{p}$ perturbation theory[18] for ZnSe. Therefore, the monotonic dependence of g from its value for ZnSe to that for cubic CdSe shows that the g-factor remains positive for the entire region of Cd content in cubic $Zn_{1-x}Cd_xSe$. For convenience in using these data, we note that a quadratic least-squares fit to the data over the whole composition range yields the relationship $g(x)=1.16-0.56x-0.18x^2$.

To model the experimental data, we have carried out calculations using an expression derived from the five-band $\mathbf{k}\cdot\mathbf{p}$ perturbation theory for the g-factor of conduction-band electrons at the Γ point:[18]

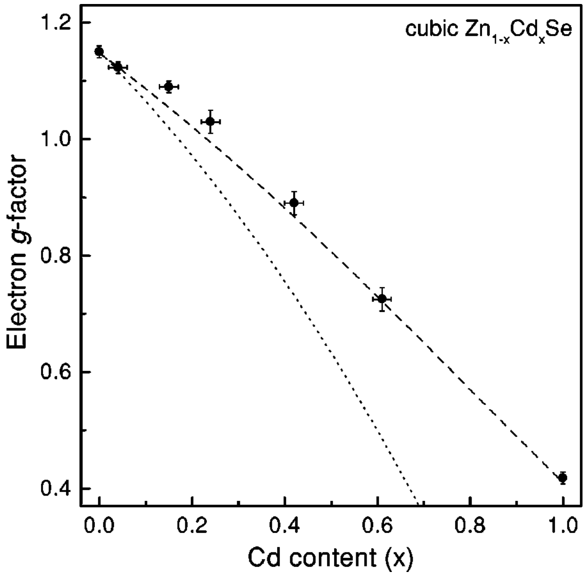

FIG. 5. Dependence of the electron g-factor for cubic $\mathrm{Zn}_{1-x}\mathrm{Cd}_x\mathrm{Se}$ on Cd content. The solid circles are experimental points. The dotted and dashed curves present the result of the calculations (see text).

$$\frac{g}{g_0}=1-\frac{P^2}{3}\left(\frac{1}{E_0}-\frac{1}{E_0+\Delta_0}\right)-\frac{P'^2}{3}\left(\frac{-1}{E_0'+\Delta_0'-E_0}+\frac{1}{E_0'-E_0}\right)+C'+\frac{2}{9}\frac{\Delta^- PP'}{E_0'-E_0}\left(\frac{1}{E_0}+\frac{2}{E_0+\Delta_0}\right),\quad (2)$$

where, in common notation, E_0, E_0', Δ_0, Δ_0', Δ^-, P, P', and $C'(=-0.02)$ are the band parameters of the material. C' is a term accounting for the effects of remote bands; it is expected to be similar in ZnSe and CdSe (Ref. 18) and, as we have shown recently,[19] gives a correction in agreement with experiment for the g-factor of the $\mathrm{ZnS}_x\mathrm{Se}_{1-x}$ system. For the calculations, a linear interpolation between the corresponding parameters of ZnSe and cubic CdSe has been used, apart from the band gap E_0, where a bowing parameter of $b=0.301$ eV in the conventional expression $E_0(x)=(1-x)E_0(0)+xE_0(1)-bx(1-x)$ was included.[11] The band parameters for ZnSe and CdSe that were used are presented in Table I. Since the values of the squared interband matrix elements P^2 and P'^2 for cubic CdSe are not available from the literature, we used first the corresponding values for ZnSe, keeping them constant over the entire region of Cd composition and only varying the band gap. The dotted curve in Fig. 5 shows the result of this calculation. A large discrepancy with the experimental data exists for $x>0.15$. The most likely reason for this discrepancy is that, as shown by Hermann and Weisbuch,[20] P^2 and P'^2 do not remain constant over the entire composition range of a ternary semiconductor. For the present case of $\mathrm{Zn}_{1-x}\mathrm{Cd}_x\mathrm{Se}$, we therefore need to obtain these parameters for cubic CdSe itself and then to make a linear interpolation over the intermediate composition range.

To estimate P^2 and P'^2 for cubic CdSe, we make use of the relationships between the effective mass and g-factor derived by Cardona[21] and apply the approach of Hermann and Weisbuch,[20] in which Eq. (2) is solved for P^2 and P'^2 simultaneously with the equation for the conduction electron effective mass, m:

TABLE I. Band parameters (in eV) for ZnSe and cubic CdSe used for the calculations.

	E_0	Δ_0	E_0'	Δ_0'	Δ^-	P^2	P'^2
ZnSe	2.821 [a]	0.403 [b]	7.33 [b]	0.09 [b]	−0.046 [c]	24.27 [c]	9.83 [c]
CdSe	1.764 [d]	0.47 [c]	6.8 [e]	0.24 [c]	−0.047 [c]	18.3 [f]	4.9 [f]

[a] From Ref. 11.

[b] From Ref. 24.

[c] From Ref. 18.

[d] Obtained by adding the hexagonal CdSe free-exciton binding energy of 15 meV (Ref. 11) to the experimentally measured free-exciton PL transition energy for cubic CdSe (present work).

[e] From Ref. 25.

[f] Estimated from the experimental values for the hexagonal CdSe electron effective mass[11] and the electron g-factor (present work) for cubic CdSe via the expression given in Eqs. (2) and (3).

$$\frac{m_0}{m}=1+\frac{P^2}{3}\left(\frac{2}{E_0}+\frac{1}{E_0+\Delta_0}\right)-\frac{P'^2}{3}\left(\frac{2}{E_0'+\Delta_0'-E_0}+\frac{1}{E_0'-E_0}\right)+C,\quad (3)$$

where m_0 is the free-electron mass and $C(=2)$ is the term accounting for remote bands.[20] In our analysis, we used the well known value $m=0.13m_0$ for bulk hexagonal CdSe.[11] There are no published data for cubic bulk CdSe and we therefore use this value rather than the recent value $m=0.112m_0$ (Ref. 22) obtained by cyclotron-resonance measurements for electrons in modulation-doped cubic CdSe/ZnSe, which has been obtained for a 10.5-nm single quantum well, rather than for bulk material. The resulting parameters are given in Table I. The use of P^2 and P'^2 estimated in this way allows us to calculate the dependence of the g-factor on the Cd content, which is now in very good agreement with the experiment (Fig. 5, dashed curve). The value of P'^2 that we obtain for cubic CdSe (4.9 eV when expressed in energy units) is approximately a factor of 2 lower than that of ZnSe; a difference of this magnitude is quite plausible [for instance, estimates of P'^2 for CdTe, CdS, and ZnS are all in the range 5–10 eV (Ref. 18)]. A good estimate of the value of P^2 (independent of the above approach) can be obtained by noting that, in the nearly-free-electron model, its value is given by h^2/a^2m_0e, where a is the lattice constant.[23] This estimate leads to a value of 16.6 eV, using a lattice parameter of 6.077 Å,[7] in reasonable agreement with the value of 18.3 eV that the above procedure yields.

We note finally that our g-factor of 0.42 ± 0.01 for cubic CdSe compares well with the values of $g_\parallel=0.6\pm0.1$ and $g_\perp=0.51\pm0.05$ obtained, respectively, for the magnetic field parallel to and perpendicular to the c axis in the hexagonal modification.[24] In Ref. 18, it was an average of these values $(g_\parallel+2g_\perp)/3=0.54$ that was used when comparing theory with experiment. This earlier paper also used the ZnSe values of P^2 and P'^2 in the analysis of CdSe, thereby obtaining a theoretical value for cubic CdSe of $g=0.23$, which is much smaller than the value we observe by SFRS. In the present work, we have been able to remove this discrepancy by using the directly measured value of the g-factor for the cubic phase of CdSe and by using consistent values of P^2 and P'^2 obtained as discussed above.

V. CONCLUSIONS

We have measured the electron g-factor in cubic $Zn_{1-x}Cd_xSe$ by SFRS over the whole composition range, including the particular case of cubic CdSe. The g-factor gradually decreases with increasing Cd content but does not change sign. An expression derived from five-band $\mathbf{k}\cdot\mathbf{p}$ perturbation theory provides an excellent description of the experimental data.

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