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Abstract

The optical absorption spectra in the region of the $4f^7 \rightarrow 4f^6 5d$ (t_{2g}) transition energies of epitaxial layers of EuTe and $Pb_{0.1}Eu_{0.9}Te$, grown by molecular beam epitaxy, were studied using circularly polarized light, in the Faraday configuration. Under σ^+ polarization a sharp symmetric absorption line (full width at half-maximum 0.041 eV) emerges on the low energy side of the band-edge absorption, for magnetic field intensities greater than 6 T. The absorption line shows a huge red shift (35 meV T^{-1}) with increasing magnetic field. The peak position of the absorption line as a function of magnetic field is dominated by the d–f exchange interaction of the excited electron and the Eu^{2+} spins in the lattice. The d–f exchange interaction energy was estimated to be $J_{df} S = 0.15 \pm 0.01$ eV. In $Pb_{0.1}Eu_{0.9}Te$ the same absorption line is detected, but it is broader, due to alloy disorder, indicating that the excitation is localized within a finite radius. From a comparison of the absorption spectra in EuTe and $Pb_{0.1}Eu_{0.9}Te$ the characteristic radius of the excitation is estimated to be $\sim$10 Å.

1. Introduction

Europium chalcogenides are prospective candidates for serving as 'spin filters' in prototype spintronic devices [1] and novel magneto-optical devices (tunable lasers, detectors and modulators) [2], where the principal source of the interesting physical properties is the d–f exchange interaction between band-edge electrons and localized Eu^{2+} spins. The optical properties of europium chalcogenides have already been investigated some 20–30 years ago, and it was established that the band-edge absorption spectrum is associated with a $4f^7 \rightarrow 4f^6 5d$ electronic transition (surveys are given in [3–6]). The experiments were performed on powders [7], polycrystalline thin layers [8] and bulk crystals [9, 10], where the

$4f^7 \to 4f^65d$ (t$_{2g}$) absorption spectrum is characterized by a very broad band—full width at half-maximum of almost ~1 eV. This absorption band was analysed by some researchers [3, 11] in terms of an excitonic transition extending mainly in the nearest neighbour Eu sites, with an exciton binding energy dependence on external fields and temperature that is governed by the d–f exchange interaction between the electron and the Eu^{2+} spins in the lattice (the magnetic exciton model). The large breadth of the absorption line, however, has remained unexplained [11], and it has led some researches to propose, instead, that the absorption spectrum is associated with a transition to extended conduction band states [4, 5, 9]. The photoluminescence of europium chalcogenides was also studied, and it is described by a broad line (full width at half-maximum FWHM = 150 meV in EuTe) with a large Stokes shift (photon energy $h\nu = 1.48$ eV in EuTe) [10].

Recently, molecular beam epitaxy (MBE) was used to produce EuTe, which has led to the observation of a much narrower photoluminescence line (full width at half-maximum FWHM = 10 meV), and at a much photon higher energy ($h\nu = 1.92$ eV) [2, 12] than in previous investigations. The photoluminescence line displays a giant red shift (34 meV T^{-1}) when a magnetic field is applied. This sensitivity was interpreted in the framework of the magnetic exciton model [3, 11]. The theory relies on such basic parameters as the d–f exchange interaction energy and effective Bohr radius, whose accepted values vary within a large interval. For example, the d–f exchange interaction energy, $J_{d-f}S$, in EuTe has been estimated to be (a) 0.35 eV, based on measurements on the temperature dependence of the optical absorption edge [4, 13], (b) 0.11 eV from the red shift of the Faraday rotation spectrum, and also of the optical band edge, when a high magnetic field is applied [14], (c) 0.17 eV from theoretical calculations [15, 16].

In this work we studied the $4f^7 \to 4f^65d$ (t$_{2g}$) optical absorption of epitaxial layers of EuTe grown by MBE, using circularly polarized light and high magnetic fields. At zero magnetic field, the optical absorption spectrum is described by a sharp threshold around 2.25 eV. When the intensity of the applied magnetic field is increased above 6 T, a very sharp symmetric absorption line (full width at half-maximum of 41 meV) appears on the low energy side of the absorption onset in one of the photon polarizations (σ^+). With increasing magnetic field this absorption line displays a huge red shift, which saturates when the Eu^{2+} spins in the crystal arrange ferromagnetically. The peak position dependence on the magnetic field fits very well into the model of a localized excitation whose energy is tunable through the d–f exchange interaction. From the absorption line shift with magnetic field we obtained an estimate of the d–f exchange interaction energy, $J_{d-f}S = 0.15$ eV, with an uncertainty less than 10%.

The optical absorption dependence on the magnetic field was also studied for a $Pb_{0.1}Eu_{0.9}Te$ sample. The optical absorption of $Pb_{1-x}Eu_xTe$ for $x > 0.6$ is EuTe-like, i.e. it is associated with an $4f^7 \to 4f^65d$ electronic transition, whose energy is pinned at 2.3 eV for $x > 0.8$ [17]. For the $Pb_{0.1}Eu_{0.9}Te$ sample, the same absorption line as seen for EuTe was detected in high magnetic fields (above 6 T); however, the maximum red shift of the line was smaller, due to a smaller concentration on Eu^{2+} in the lattice. In addition, the width of the absorption line (43 meV) was larger than for EuTe (41 meV). Assuming that the increase in the breadth of the line is due to alloy disorder, the radius of localization of the excitation is estimated to be ~10 Å.

Recent investigations of the photoluminescence spectrum of EuTe grown by MBE have discovered almost the same red shift of the optical line (34 meV T^{-1}) when a magnetic field is applied, as in this work. It should be pointed out, however, that the physical mechanisms involved in the photoluminescence could be much more complex than in the optical absorption. According to the Franck–Condon principle [18], whereas absorption occurs when the crystal lattice is undistorted, emission occurs when the atoms surrounding the excitation move to their

new equilibrium positions, and in EuTe a large distortion occurs due to the a large charge transfer from to excited Eu^{2+} to the surrounding atoms [3]; in addition to the mechanical distortion, an alignment of the Eu^{2+} spins inside the excitation radius (forming a magnetic exciton) would also contribute to reducing the energy of the excitation. The amount by which the energy is reduced could be dependent on the intensity of the magnetic field applied, due to the changing size of the excitation, making the magnetic field induced red shift seen in the PL much more complex than the red shift of the absorption spectrum reported in this work, in which the positions of the atoms in the lattice, and their spin orientations, are fixed at the unperturbed crystal state.

2. Experimental details

EuTe and $Pb_{0.1}Eu_{0.9}Te$ epitaxial layers (~1.1 μm thick) were grown by molecular beam epitaxy (Riber 32P MBE) on freshly cleaved (111) BaF_2 substrates. In the case of EuTe, the constituents (Eu and Te) were sublimated from elemental sources, while a PbTe source was used for the $Pb_{0.1}Eu_{0.9}Te$ growth. $Pb_{1-x}Eu_xTe$ crystallizes in the rock salt structure, and its lattice mismatch to the BaF_2 substrate (fluoride structure) varies from 4% to 6%, with increasing Eu content in the ternary compound. In addition, the thermal expansion coefficient of BaF_2 is well matched to those of PbTe and EuTe, thus preventing the build-up of high thermal strains when cooling the samples to cryogenic temperatures. The Eu content values in the $Pb_{0.1}Eu_{0.9}Te$ sample was determined by magnetization SQUID measurements, with an estimated uncertainty of less than 1%. The crystalline quality was investigated by measuring the x-ray rocking curve of the (222) Bragg reflection of the samples. The peak position corresponded to the bulk lattice parameter of 6.600 Å, and the full width at half-maximum of the EuTe diffraction peak was about 400 arcsec, which is indicative of a good structural quality (for $Pb_{0.1}Eu_{0.9}Te$ the FWHM of the peak was larger than in EuTe by about 100 arcs, due to alloy disorder). PL measurements at $T = 2$ K were made, using the 488 nm line of an Ar laser, and the sharp luminescence (FWHM $\sim$ 10 meV) at 1.922 eV was detected, demonstrating the high optical quality of the samples [2, 12]. The optical absorption spectra of EuTe samples and $Pb_{0.1}Eu_{0.9}Te$ were measured at 1.8 K, using left and right circularly polarized light, in magnetic fields of intensity up to 17 T. The sample (square shaped, of side length 2.5 mm), was immersed in superfluid helium, and light was conveyed to the sample, and collected from the sample, in the Faraday configuration, using optical fibres coupled to *in situ* miniature focusing optics and circular polarizers.

3. Results

The absorption spectrum taken at zero field shows the characteristic absorption onset at $\sim$2.3 eV (see figure 1), which is associated with the $4f^7 \rightarrow 4f^65d$ (t_{2g}) transition [4, 5]. In the transparency region, the absorption coefficient shows weak oscillations, due to the effect of Fabry–Perot interference in the thin epitaxial film.

When a magnetic field is applied, the absorption edges taken in the two polarizations show remarkably different behaviours. In the σ^- polarization we measure a red shift of the absorption edge, which saturates when the applied field, B_a, reaches 8.3 T. In the σ^+ polarization, however, the absorption spectrum does not red shift as a whole, but develops a new sharp absorption peak that emerges from the main absorption edge. With increasing magnetic field the new absorption peak gains intensity, and it red shifts, until saturation is reached at $B_a = 8.3$ T. The same absorption spectra were measured for a number of EuTe samples of various thickness
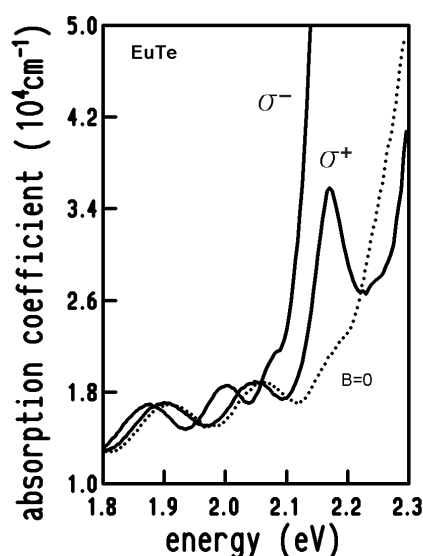
Figure 1. Absorption spectra of EuTe for $B = 0$ T (dotted curve) and $B = 9.6$ T (full curves), in the latter case the polarization corresponding to each curve (σ^+ or σ^-) is indicated.

in the range of 1–3 μm, some of which contained a BaF_2 protective layer, some of which did not. The position and width of the peak were the same for all samples, and the optical density of the sharp absorption peak was proportional to the thickness of the EuTe epitaxial layer, demonstrating that the absorption line is originated in the bulk of the EuTe.

For our sample geometry (a thin layer of EuTe subject to a perpendicular magnetic field), the internal field will be given by $B_{int} = B_a - \mu_0 M$, where M is the magnetization of the sample, and $\mu_0 M$ varies linearly with B_a and saturates to $\sim$1.1 T at $B_{int} = 7.2$ T [19], meaning that $B_a = 8.3$ T corresponds to an internal field equal to the well-known critical field value of 7.2 T for EuTe. We have employed fields as large as 17 T, but no further changes were seen in the absorption spectra. The absorption spectra at $B_a = 9.6$ T in both polarizations are shown in figure 1.

To show the evolution of the absorption spectra taken in the σ^+ and σ^- polarizations when the applied magnetic field is increased from zero, a contour plot of the absorption spectra is shown in figure 2. This figure shows that in the σ^- polarization the absorption edge red shifts almost linearly with the field intensity, until saturation is reached. In contrast, the evolution of the absorption spectrum in the σ^+ polarization does not show a linear red shift of the absorption edge, but rather the changes in the spectrum are described by the emergence of a sharp absorption line on the low energy side of the spectrum. When B is less than the saturation value, the strength of the sharp absorption line increases with B, and it red shifts, leading to a completely resolved line at the highest fields. The red shift of the sharp peak is described by a huge value of 35 meV T^{-1}, which is about the same value as seen in the shift of excitonic PL [2, 12]. Notice also that the main absorption edge remains in nearly the same place as at $B = 0$.

The peak position and full width at half-maximum of the sharp absorption peak seen in the σ^+ polarization at fields above 8.3 T were obtained from a fit of the absorption spectrum with a linear combination of a Gaussian curve and a straight line (see figure 3). For EuTe, the maximum occurs at 2.169 eV (the peak is shifted by $\sim$0.22 eV from the main $4f^7 \rightarrow 4f^6 5d$ (t_{2g})
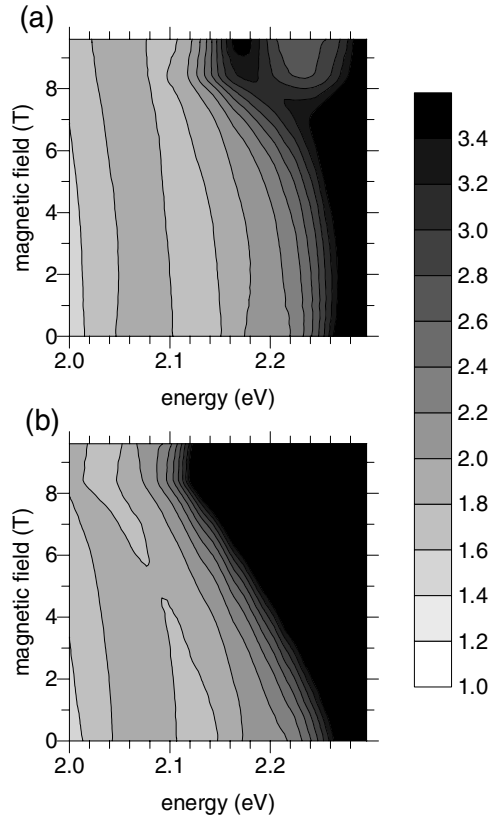
Figure 2. A contour plot for the absorption spectrum dependence on the magnetic field intensity: (a) σ^+; (b) σ^-.

absorption), and the full width at half-maximum (FWHM) equals 41 meV. The $Pb_{0.1}Eu_{0.9}Te$ sample showed the same qualitative behaviour as seen in EuTe, but the low energy side peak was broader than for EuTe, and centred at a higher energy, as shown in the right panel of figure 1. The absorption maximum is seen at 2.181 eV, i.e. an energy 12 meV greater than for EuTe, and the FWHM = 43 meV, greater by 2 meV compared to the corresponding value for EuTe (see the right panel in figure 3).

4. Discussion

The magnetic field dependence of the newly discovered absorption line will be discussed in the framework of the d–f exchange interaction. The d–f exchange interaction energy operator is given by [3]

$$H_{df} = -J_{df} \sum_{n\mu\nu} a_{n\mu}^{\dagger} a_{n\nu} S_n \cdot \sigma_{\mu\nu}$$

where J_{df} is the d–f exchange interaction constant, $a_{n\mu}^{\dagger}$ is the creation operator of a Wannier function centred at the nth Eu^{2+} with spin μ, σ is a Pauli spin operator and S_n is the spin of the nth Eu^{2+}. We treat H_{df} as a perturbation over a photoexcited electron in a d band with definite spin, whose wavefunction is given by $\Psi = \sum_n c_n a_{n\chi}^{\dagger} |0\rangle$. The spin of the photoexcited
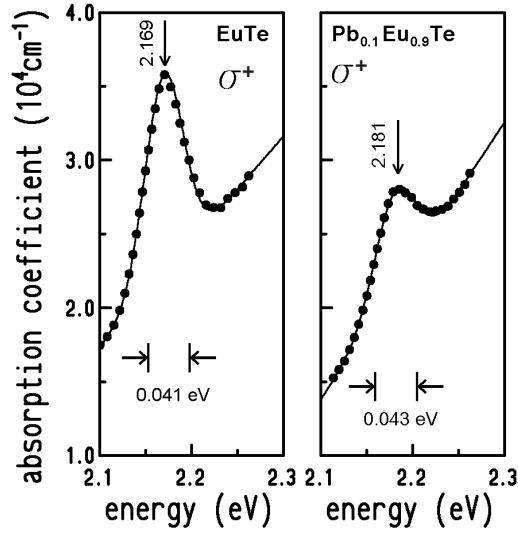
Figure 3. Dots represent the σ^+ absorption spectrum of EuTe (left) and $Pb_{0.1}Eu_{0.9}Te$ (right) measured at $B = 9.6$ T. Full curves are fitting curves for the measured spectra.

electron is subject to the constraint that it must be parallel to the Eu^{2+} spin at the site where the excitation occurred [3, 13]. We assume that the wavefunction describing the excited state encloses a large number of Eu^{2+} sites; hence at zero magnetic field ($T = 0$ K), when the arrangement of the Eu ions is antiferromagnetic (the Eu spins lie in the (111) plane [19]), the d–f interaction energy of the photoexcited electron averages out to zero. As the magnetic field applied normal to the (111) increases, the Eu^{2+} spins cant in the magnetic field direction, the d–f exchange interaction energy increases and at arbitrary field it will be given by

$$\Delta E_{df} = -J_{df} S \cos^2 \theta \tag{1}$$

where 2θ is the angle between the sublattice spin directions, determined by [9]

$$\cos \theta = \begin{cases} \dfrac{B_{int}}{B_{Sat}} & \text{if } B_{int} < B_{Sat} \\ 1 & \text{if } B_{int} > B_{Sat} \end{cases}$$

where $B_{Sat} = 7.22$ T is the saturation field for EuTe [19].

Figure 4 shows the measured position of the side peak as a function of applied magnetic field both for EuTe and for $Pb_{0.1}Eu_{0.9}Te$. The same peak position dependence on magnetic field as for the EuTe sample shown in figure 4 was obtained for a second EuTe sample whose epitaxial layer thickness was 1.75 μm. The solid curves in figure 4 were obtained by simultaneous fitting of all of the experimental values shown to the equation

$$E = E_0 + x \Delta E_{df} \tag{2}$$

where E_0 is the position of the excitonic line at $B = 0$, x is the molar fraction of Eu in the $Pb_{1-x}Eu_xTe$ sample and ΔE_{df} is given by equation (1). Equation (2) should be valid in the range $x > 0.8$, where the $Pb_{1-x}Eu_xTe$ gap is EuTe-like and nearly constant [17]. In the fitting procedure, the spin of the Eu^{2+} was fixed at $S = 7/2$, and the d–f exchange interaction constant, J_{df}, and E_0 were the fitting parameters, leading to the best fit values of $E_0 = 2.321$ eV and $J_{df}S = 0.15 \pm 0.01$ eV.

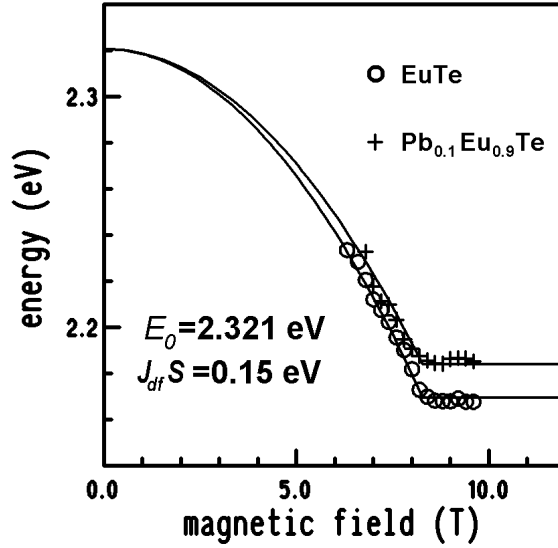**Figure 4.** The magnetic field dependence of the energy position of the maximum in the 4f^7 → 4f^{6}5d (t$_{2g}$) excitonic absorption measured in σ^+ polarization.

For Pb$_{0.1}$Eu$_{0.9}$Te, the energy position of the side peak is greater than in EuTe, which is due to a lower density of spins in the lattice. Then, assuming that in going from EuTe to Pb$_{0.1}$Eu$_{0.9}$Te, the increase in the FWHM of the side peak is due to inhomogeneous broadening, caused by random fluctuations in the local Eu concentration, the number of Eu^{2+} spins inside the exciton radius can be estimated through

$$N = \frac{8x(1-x)\left(\Delta E_{\max}/\Delta x\right)^2 \ln 2}{\left(\text{FWHM}_{\text{Pb}_{1-x}\text{Eu}_x\text{Te}}\right)^2 - \left(\text{FWHM}_{\text{EuTe}}\right)^2}$$

where $\Delta E_{\max}$ and Δx are the shift in the position of the maximum of the excitonic line and the change in Eu molar fraction on going from EuTe to Pb$_{1-x}$Eu$_x$Te, respectively. Using the results obtained for EuTe and Pb$_{0.1}$Eu$_{0.9}$Te, we find $N = 42$, which justifies the assumption made above that the exciton is large, and means that the exciton sphere encloses about ten conventional unit cells of the fcc structure. This estimate puts the exciton diameter at approximately 18 Å.

In conclusion, we have studied the optical band-edge absorption in EuTe and Pb$_{0.1}$Eu$_{0.9}$Te grown by MBE at low temperatures and high magnetic fields. Under σ^+ polarization, we detect a well-resolved sharp peak (full width 0.041 eV). The sharp absorption line displays a huge red shift of about 35 meV T^{-1} when the magnetic field increases, and its separation from the main absorption band reaches ~0.2 eV at the saturation field. For Pb$_{0.1}$Eu$_{0.9}$Te, the same absorption line was also detected, but it is broader, which is an indication of a localized excitation. The displacement of the absorption line with magnetic field fits very well into a model of a localized excitation whose energy is tuned by the d–f exchange interaction. From a fit of the experimental points to the theory we obtain a direct estimate of the d–f exchange interaction energy, $J_{\text{df}}S = 0.15 \pm 0.01$ eV.

Acknowledgments

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