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High energy sideband on the magnetic polaron related luminescence in EuTe

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We investigated the near band gap luminescence of EuTe thin films grown by molecular beam epitaxy, using excitation intensities up to 2×10^5 W/cm^2. Besides the previously reported high energy emissions MX$_1$ and MX$_2$, we observed an additional emission band at higher energies. This higher-energy band is only detected when high excitation intensities, over 2 kW/cm^2, are used. With increasing externally applied magnetic field, this additional emission band shifts to lower energies at a rate even higher than the MX$_1$. The two bands, however, have different temperature dependences and decay times, suggesting that distinct electronic states are involved in their emission. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4748981]

Magnetic semiconductors (MS) play a central role in spintronics[1] and have attracted significant attention in the past two decades, in an effort to reach a deeper understanding of their properties and find practical applications. MS can also be used in magneto-optical devices, due to the strong dependence of their electronic and optical properties on applied magnetic field. Intrinsic MS, like the Europium-monochalcogenides EuX (X = O,S,Se,Te), are particularly well suited for opto-electronic and spintronics applications because they have densities of magnetic ions higher than the diluted MS. In consequence, in intrinsic MS the electronic and optical properties usually depend stronger on applied magnetic field than in diluted MS like Mn-doped III-V and II-IV compounds. The EuX are also interesting because they are classical Heisenberg magnets, where the magnetic interactions are well modeled, and can be used to advance our basic understanding of the MS.[2]

The EuX have been studied since the 60 s,[2] and recently they have attracted attention both from the experimental and theoretical communities due to their interesting properties, like their complex band structures,[3,4] the formation of magnetic polarons,[5,6] the appearance of narrow absorption lines in EuTe,[7] the generation of optical second harmonics in EuTe and EuSe,[8] and the possibility of growing self-assembled quantum dots of EuTe by molecular beam epitaxy (MBE),[9] among others.

Among the EuX, has the wider energy gap (Eg ~ 2.2 eV at 2 K), which makes it the best suited for optical applications in the visible spectral range. EuTe has anti-ferromagnetic (AF) order below T$_N \sim 9.6$ K. The optical properties of EuTe depend strongly on applied magnetic field due to the strong exchange-interaction between the electrons in the conduction band and the Eu^{2+} localized magnetic moments (S = 7/2), which is reflected in the complex band structure of EuTe.[4] For instance, the major intrinsic optical emission band observed in high-quality EuTe films at low temperatures, the MX$_1$ emission, has an energy shift rate with applied magnetic field as high as -34 meV/T in Faraday

geometry,[10–12] and -40 meV/T in Voigt geometry. Based on theoretical results,[4] the MX$_1$ emission band in EuTe (at ~ 1.92 eV) has been attributed to a magnetic polaron induced radiative transition involving conduction band electrons at the X(1,0,0) point in reciprocal space and localized holes in the quasi-dispersionless *4f*-levels of Eu coupled by the exchange-interaction.[13] The MX$_1$ band is usually accompanied by a satellite band named MX$_2$ (at ~ 1.88 eV), attributed to its magnon-replica.

The AF ordering of EuTe has restricted its uses in spintronics till now, because in most spintronics devices, like spin-valves, AF materials have been only used in secondary passive roles like pining the magnetization of a ferro-magnet.[14] However, the recent development of a spin-valve-like device based on an AF/non-magnetic junction,[15] and the possibility of room temperature anti-ferromagnetism, for instance in I-Mn-V semiconductors,[16] promise a wider use of AF semiconductors in spintronics.[17]

In this work, we report the observation of an additional high-energy emission band in high quality EuTe that is only visible for high excitation intensities (above ~ 2 kW/cm^2). This additional high energy band (named HE band hereafter) has a decay time more than fifteen times shorter than the MX$_1$ and also shows a weaker dependence on temperature. Besides, the HE band presents a giant Zeeman splitting, similarly to the MX bands, with a shift rate of ~ -40 meV/T, which indicates a strong electron Eu^{2+} magnetic-ion exchange-interaction.

The investigation of the high-energy emission reported here provides further information about the complex electronic structure of EuTe and could assist in the theoretical calculations for that interesting material and its alloys.

The EuTe epitaxial films were grown in a Riber-32p molecular beam epitaxy (MBE) system on freshly cleaved (111) BaF$_2$ substrates. The substrate temperature during growth was $230\,°$C and the deposition rate, 1.4 Å/s with a Te/Eu flux ratio of ~ 3.5. In this work we present the results from a 1.3 μm thick EuTe film that was capped with 80 nm of MBE-grown BaF$_2$ to prevent oxidation. The capping layer should not influence the optical measurements because BaF$_2$ is

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transparent in the investigated spectral range. The sample used has a fairly good crystalline quality, with a full width at half maximum of the x-rays rocking curve around the (222) reflection of 360 arc sec.

We investigated the EuTe photoluminescence (PL) in continuous-wave (CW) and time-resolved (TR) regimes, with externally applied magnetic fields in Faraday geometry up to 10 T, and temperatures ranging from 2 to 100 K. The CW-PL measurements were performed using a 488 nm Ar^+ laser line focused by a $50\times$ microscope objective that produces a spot at the sample surface $\sim2\,\mu m$ in diameter. The luminescence was detected by a 64 cm monochromator with a 600 g/mm grating and a Si CCD. The TR-PL was performed using a 410 nm laser pulse for excitation (second harmonic of a ps Ti:Saphire laser), a Hamamatsu Streak Scope for detection and a continuous-flow He cryostat. The laser spot at the sample surface for these measurements was $\sim200\,\mu m$ in diameter. We also measured the optical transmittance of the sample using a halogen lamp as white light source and the same magneto-cryostat used for CW-PL. In this case the spot size was ~1 mm in diameter.

The EuTe film CW-PL spectra at 4 K for several excitation intensities is shown in Fig. 1. The PL spectrum for the lowest excitation intensity only exhibits two bands, at 1.916 eV and 1.877 eV, respectively. These energies are the same reported by Heiss *et al.* for the MX_1 and MX_2 bands.[11,12] These bands are attributed, respectively, to magnetic polaron induced near-band gap luminescence and its magnon replica. For excitation intensities larger than $\sim1\,kW/cm^2$, an experimental condition easily obtained in a micro-PL setup, an additional emission band that we named HE appears at 1.976 eV. With no magnetic field applied, the HE transition is Stokes-shifted with respect to the energy band gap by ~265 meV. The HE band in EuTe has not been

reported before probably because the excitation intensities used in previous studies were below $1\,kW/cm^2$. With increasing excitation intensity the HE band increases its intensity faster than the MX_1, reaching almost half the MX_1 height. What appears to be a second magnon replica of the MX_1 band, labeled MX_3 in Fig. 1, is also observed at low temperatures. Finally, it is worth noticing that the energy separation between the MX_1 and HE bands (~60 meV) is larger than the separation between the MX_1 and MX_2 (~40 meV).

Fig. 2(a) shows a series of PL spectra measured at different temperatures from 4 K to 100 K. In all cases the excitation intensity was $20\,kW/cm^2$. The resulting PL peak energies and integrated intensities are shown in Figs. 2(b) and 2(c). Distinct behaviors with increasing temperatures are observed for the HE and MX_1 band. The MX_1 band shows a strong blue shift that starts abruptly around the Néel temperature ($T_N = 9.6$ K) and persists up to ~30 K. At the same temperature range, the MX_1 band intensity markedly decreases (Fig. 2(c)). The HE band, on the other hand, is less sensitive to temperature variations. For temperatures between 2 K and ~17 K its position shows a small red shift of ~5 meV, and for temperatures larger than ~20 K it exhibits a linear blue shift with a slope of ~0.18 meV/K. The intensity of the HE band slightly increases in the 2 K–35 K range, and for higher temperatures it decreases. The HE band is still visible at temperatures up to 100 K, while the MX_1 band is no longer detectable above 40 K.

The blue shift of the MX_1 band for temperatures above T_N is qualitatively explained by the photo-induced localized
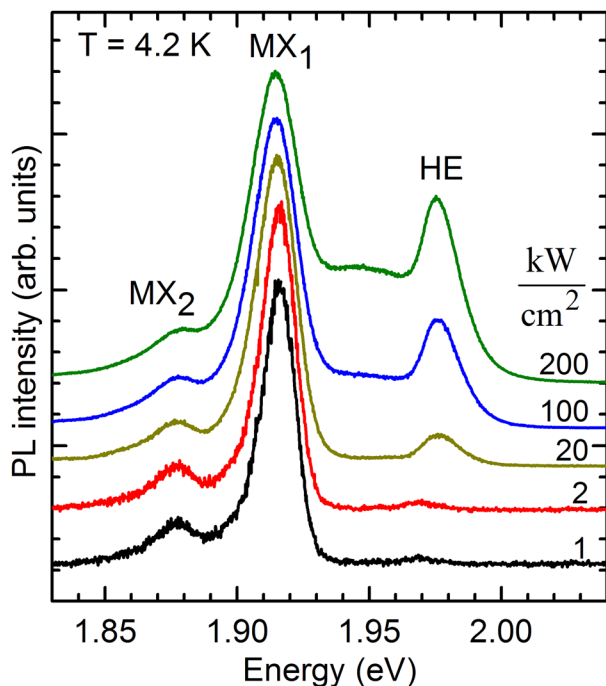

FIG. 1. Normalized CW-PL spectra of the epitaxial EuTe film measured at 4.2 K for different laser intensities. The curves were shifted vertically for clarity.

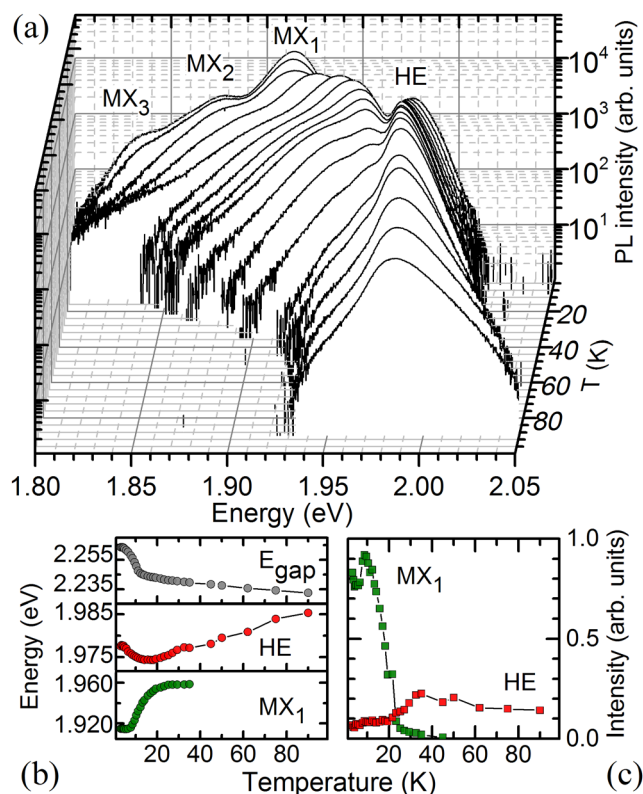
FIG. 2. (a) CW-PL spectra of EuTe at different temperatures up to 100 K. An excitation intensity of $20\,kW/cm^2$ was used in all cases. (b) PL peak positions and band gap absorption edge vs. temperature. (c) Integrated PL intensity of the MX_1 and HE bands vs. temperature.

magnetic polaron (PILMP) model,[5] which takes into account the electron-ion (*d-f*) exchange-interaction, the electron-hole Coulomb interaction, as well as the phonon interaction. The HE band, on the other hand, has a behavior with temperature not so closely matched to the model of a PILMP in EuTe. Most noticeable, the HE peak energy shifts only slightly as temperature rises above the Néel temperature, while its intensity decays slowly, not abruptly as occurs with the MX_1.

Fig. 2(b) also shows the absorption-edge energies obtained by transmittance spectroscopy using the same procedure used by Heiss *et al.*[13] The absorption edge energy shows a red shift with increasing temperatures in the whole measured temperature range. The shift rate, however, abruptly changes at T_N, an indication of its magnetic-order dependence. Using the absorption edge as an estimative of the EuTe band gap energy, we obtain different but significantly large, Stokes-shift energies for the MX_1 and HE bands. The large Stoke shifts energies in EuTe are usually attributed to different conduction bands involved in the absorption and emission processes, but they can also include magnetic polaron binding energies.

The effects of an externally applied magnetic field on the emission and absorption spectra were also investigated. The field was applied perpendicular to the epitaxial layer (Faraday configuration). The PL spectra of EuTe for different magnetic fields up to ∼8 T is shown in Fig. 3(a). The excitation intensity was 20 kW/cm^2 in all cases.

Considerable red shifts are observed for all emission bands as the magnetic field increases. The MX_1 emission shifts almost linearly up to ∼7 T, with a rate of −34 meV/T, in agreement with previous results.[11,12,18] The large red shift of the MX_1 has its origin in the giant Zeeman-splitting effect

due to the strong exchange-interaction between electrons and Eu^{2+} magnetic ions.[11,12] Remarkably, the behavior of the HE band, while different as a function of temperature, is very similar to the MX_1 behavior as a function of applied magnetic field. Moreover, the HE band displays a linear red shift of −40 meV/T, which is even larger than for the MX_1 band. The high shift rate of the HE band with magnetic field indicates that the states involved in its emission also experience a strong electron Eu^{2+} magnetic-ion exchange-interaction. With increasing magnetic field, the intensity of the HE and MXs bands decreases steadily, and they almost vanish when full FM ordering has been reached at ∼7 T. As with the MXs bands, the decrease of the HE band intensity with applied magnetic field suggests its dependence on the formation of magnetic polarons.

With increasing magnetic field, the absorption edge obtained by transmittance measurements also shifts to lower energies. However, unlike the emission lines that shift linearly with magnetic field up to the saturation value of ∼7 T, the absorption edge shifts quadratically, and the total energy variation is smaller (∼100 meV at 8 T). This results also agrees with previous reports.[12,19]

The behavior of the HE band suggests that the emission process involves electrons in the conduction band and strongly localized holes in the Eu^{2+} 4f levels. These electrons must be initially at higher energy states than the ones involved in the MX_1 emission, and also at energies lower than the band gap. A possible origin of the HE band is revealed by the calculated EuTe bands structure,[4] where the lowest conduction band shows a local energy minimum, located in reciprocal space, in the (0,0,0)-(0,0,1) direction approximately at one third from the center of the Brillouin zone to the border. The energy of that intra-zone local minimum is slightly higher than the energy of the absolute minimum at the X-point in reciprocal space, which is related to the MX_1 emissions. If the HE band came from carriers accumulated at the local minimum that would explain not only the HE band energy position but also why it is only detectable using high power-density excitation. Furthermore, the electrons at this local minimum will quickly relax to the lower energy state at the X-point. To address this point, we measured the TR-PL of the HE and MX_1 bands.

Fig. 4(a) shows the evolution of the PL spectra with time. The curves are obtained by integrating the TR-PL in 25 ps intervals, each delayed by a multiple of 25 ps. It is apparent that the HE band emission starts before the MX_1 and its intensity rises and falls before the MX_1 reaches its maximum intensity. Both bands positions show small red shifts with increasing delay time (Fig. 4(a) inset). This red shift occurs in a short time interval and saturate in ∼300 ps. Similar red shifts have been observed in diluted magnetic semiconductors, for instance in quantum dots of $Cd_{1-x}Mn_xTe$ (Ref. 20) and attributed to the formation of magnetic polarons.

Fig. 4(b) shows the time evolution of the integrated PL intensity of the MX_1 and HE. Both bands show mono-exponential intensity decays, but with rather different decay times. The MX_1 have a decay time of ∼1.5 ns, in agreement with previous results,[13] while the HE have a much shorter decay time of ∼90 ps (detailed in Fig. 4(c)). The distinct time evolution for these two emissions is consistent with the
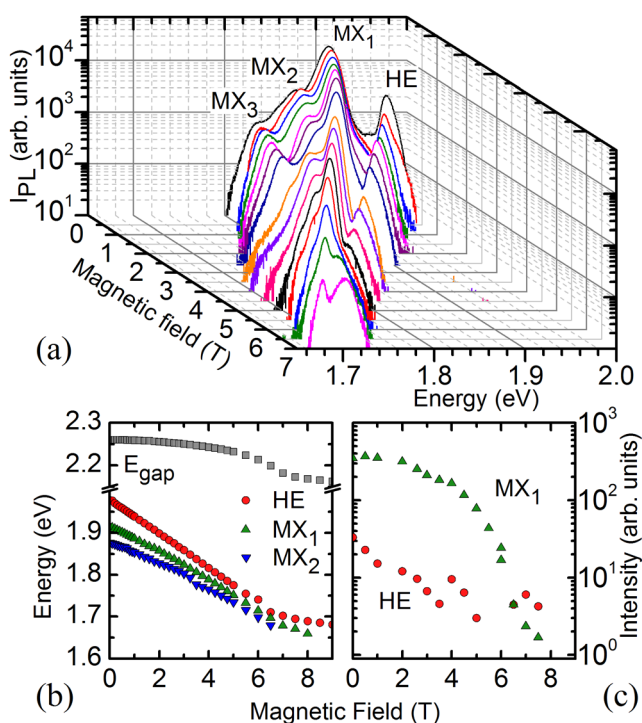

FIG. 3. (a) CW-PL spectra of EuTe at 5 K for various applied magnetic fields. (b) PL peak positions and absorption edge vs. magnetic field. (c) Integrated intensity vs. magnetic field.
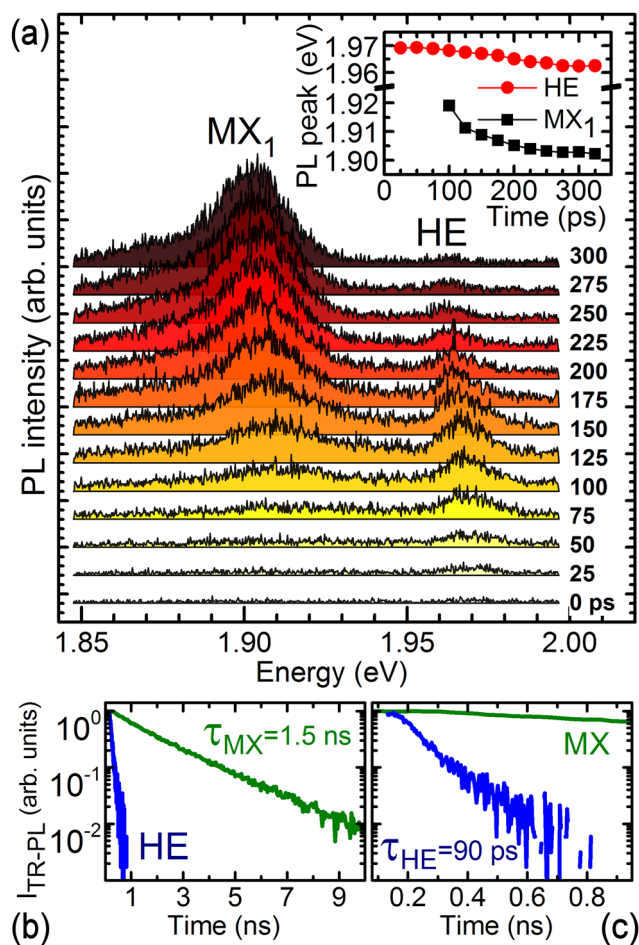
FIG. 4. TR-PL of EuTe at 7 K. (a) Evolution of the PL spectra with time. The curves are obtained by integrating the TR-PL in 25 ps intervals, each delayed by a different amount of time, from t = 0, which do not necessarily correspond with the excitation pulse. The inset shows the MX₁ and HE peak energies vs. time. (b) Decay in time of the MX₁ and HE integrated intensities. The curves have been normalized and shifted to ease comparison. (c) Same as (b), but zooming on the region below 1 ns to better resolve the HE decay.

fast transference of electrons from the local minimum to the X-point, as discussed above.

The observed red shifts evolutions of the HE and MX₁ bands after the pulsed excitation as well as the strong dependence of their peak position with applied magnetic field, suggest that both emissions are magnetic polarons induced. However, for the HE band the question remains open, since its thermal behavior is different from that of the MX bands. The distinct thermal behavior of the HE band may be related to the specific electronic states involved in its emission or to its shorter lifetime, among other factors. Further investigations are necessary to elucidate this point.

In summary, we studied the PL spectra of a EuTe thin film using high excitation intensities and found an optical emission, the HE band at energies higher than the MX₁ band

commonly observed in high quality EuTe. The HE band behavior suggests that it originates from radiative transitions involving electrons from an intra-zone local energy minimum of the lowest EuTe conduction band and holes in the Eu^{2+} 4f levels. With applied magnetic field the HE band shifts to lower energies at a rate even higher than the MX₁, which indicates a strong electron Eu^{2+} magnetic-ion exchange-interaction, and the possibility of magnetic polarons formation. However, if magnetic polarons are involved in the HE emission, the difference between its behavior with temperature and that of the MX₁ has yet to be explained. These results can stimulate further experimental and theoretical investigations of the complex electronic structure and optical properties of the EuX. Also, the existence of an electronic transition that remains optically active at liquid nitrogen temperature increases the chances of EuTe being used in prototype opto-electronic and spintronics devices.

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