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Magnetic linear dichroism in absorption spectroscopy of EuTe

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Abstract

The magnetic linear dichroism (MLD) at band-edge photon energies in the Voigt geometry was calculated for EuTe. At the spin-flop transition, MLD shows a step-like increase. Above the spin-flop transition MLD slowly decreases and becomes zero when the averaged electronic charge becomes symmetric relative to the axis of light propagation. Further increase of the magnetic field causes ferromagnetic alignment of the spins along the magnetic field direction, and MLD is recovered but with an opposite sign, and reaches maximum absolute values. These results are explained by the rearrangement of the Eu^{2+} spin distribution in the crystal lattice as a function of magnetic field, due to the Zeeman interaction, demonstrating that MLD can be a sensitive probe of the spin order in EuTe, and provides information that is not accessible from other magneto-optical techniques, such as magnetic circular dichroism measurement studies.

1. Introduction

Europium chalcogenides (EuX) are magnetic semiconductors that have attracted much interest because of the large magnetic moment associated with the sites occupied by europium ($S = 7/2$), combined with a wide bandgap with a transparency window in the visible range of the optical spectrum. It was envisaged early on that magneto-optical modulators could be built from EuX if the spin order could be controlled externally [1], and, more recently, EuX has been suggested as a prospective candidate for applications in spintronic devices and various other applications [2, 3]. Progress in the applications of EuX in technology will benefit from a detailed knowledge of the electronic energy spectrum and the associated magneto-optical properties of EuX, which despite many years of research are still not completely understood.

A fundamental manifestation of the band-edge electronic energy structure is the optical absorption spectrum. It has been widely accepted that the band-edge optical absorption in EuX arises due to electronic transitions from electronic levels strongly localized at the Eu sites, to a conduction band built from $5d(t_{2g})$ Eu atomic levels split by the crystal field of octahedral symmetry (the so-called $4f^7(^8S_{7/2}) \rightarrow 4f^6(^7F_J)5d(t_{2g})$ model). However, early calculations of the absorption spectrum in EuX, based on this model, have not found good agreement with experiments [4]: a central difficulty is that experimentally only very broad absorption bands (widths of the order of $\sim$1 eV) are observed in EuX, whereas the theoretical model predicted absorption lines on a much finer scale. The absence of detailed agreement between theory and experiment was ascribed to many-body effects, not included in the one-particle picture implied in the theory used [5].

Only recently has a more complete picture of the mechanisms and processes that give rise to the observed experimental spectrum become possible: the absorption spectrum within the $4f^7(^8S_{7/2}) \rightarrow 4f^6(^7F_J)5d(t_{2g})$ model was re-examined [6–8] for EuTe, taking into account the presence of antiferromagnetic spin domain formation at zero field and the realignment of the spins in these domains when a magnetic field is applied externally. The extended model explained the absence of resolved lines at zero magnetic field. For complete ferromagnetic order, induced by a strong external magnetic field, absorption experiments carried out in the Faraday geometry showed sharp lines, together with a large magnetic circular dichroism, and all observations were well described by the theory. The calculated magnetic circular dichroism (MCD) showed very good agreement with the experimental results [7], up to 400 meV above the optical band edge of EuTe, which suggests that the theoretical model could be used to foresee as yet unexplored optical properties of EuTe.

In the present study we examined theoretically the magnetic linear dichroism (MLD) in the Voigt geometry, within the framework of the same $4f^7(^8S_{7/2}) \rightarrow 4f^6(^7F_J)5d(t_{2g})$ model,

including the effects of existence of complex spin domain evolution as a function of applied magnetic field. MLD is defined by the ratio

$$\mathrm{MLD} = \frac{\alpha^{\parallel} - \alpha^{\perp}}{\alpha^{\parallel} + \alpha^{\perp}},$$

where $\alpha^{\parallel}$ ($\alpha^{\perp}$) is the optical absorption coefficient of light that is plane polarized in a direction parallel (perpendicular) to the magnetic field, which is applied at a right angle to the light wavevector. MCD is defined by a similar formula:

$$\mathrm{MCD} = \frac{\alpha^{+} - \alpha^{-}}{\alpha^{+} + \alpha^{-}},$$

where the Faraday geometry is assumed (the magnetic field is applied in the direction of the light wavevector), and α^{+} (α^{-}) is the optical absorption coefficient of light that is circularly polarized according to the right-hand (left-hand) rule.

Because circularly polarized light carries angular momentum, whereas linearly polarized light does not, fundamental differences between MCD and MLD arise, and MCD and MLD reflect different physical characteristics of the system under study. While MLD measures the anisotropy of the electronic charge distribution in the plane perpendicular to the direction of light travel, MCD is only non-zero when inversion symmetry is absent, and in a crystal with structural inversion symmetry, such as EuTe, MCD will reflect the degree of magnetization in the direction of light travel. Therefore, for instance, MCD is always zero for antiferromagnetic EuTe, but MLD is not necessarily so. Moreover, the value of MLD is insensitive to a reversal of the spin direction; therefore it will remain the same for either an antiferromagnetic or ferromagnetic spin distribution, as long as the axes along which the spins lie are unchanged.

These considerations have important consequences for EuTe. It is well known that the EuTe structure undergoes a spin-flop transition at around a magnetic field of intensity $B \sim 0.08$ T [9]. Both below and above the spin-flop transition, the arrangement of the spins is antiferromagnetic; therefore the MCD signal remains zero. However, because MLD is sensitive to the changes in the orientation of the spin sublattices, our study shows that the MLD signal should present a sudden increase at the spin-flop transition; thus MLD could be used as a sensitive probe of the spin order in EuTe.

At fields above the spin-flop transition, the magnetizations of the two sublattices continuously tilt towards the direction of the magnetic field, until ultimately complete ferromagnetic arrangement is achieved at the saturation field of 7.2 T [10]. While it is known that MCD shows a continuous increase until saturation is reached at the ferromagnetic arrangement [7, 8], here we find that MLD displays a very different behaviour, i.e., it decreases above the spin-flop transition, becomes nearly zero at a critical field when the spin orientation becomes symmetric relative to the direction of light propagation, and then increases with a reversed sign, up to the saturation field.

2. Model

To calculate the absorption spectrum in the Voigt geometry we follow the theoretical framework described by us previously [8], used to calculated the absorption spectrum in the Faraday geometry. Absorption is associated with electronic transitions between the ground $^8\mathrm{S}_{7/2}$ state and a final state in which the Eu ionic core is left in a $^7\mathrm{F}_J$ state ($J = 0, \ldots, 6$), split by the Landé interval rule, and an electron in a narrow $5\mathrm{d}(\mathrm{t}_{2\mathrm{g}})$ conduction band. In the tight binding approximation, the $5\mathrm{d}(\mathrm{t}_{2\mathrm{g}})$ conduction band Bloch state, of energy $E_X(\boldsymbol{k})$, is given by

$$\Psi(\boldsymbol{k}, \boldsymbol{r}) = \frac{1}{\sqrt{\mathcal{N}}} \sum_{\boldsymbol{R}} \mathrm{e}^{\mathrm{i}\boldsymbol{R}\cdot\boldsymbol{k}} X(\boldsymbol{r} - \boldsymbol{R}), \tag{1}$$

where $X(\boldsymbol{r}-\boldsymbol{R})$ represents one of the $5\mathrm{d}(\mathrm{t}_{2\mathrm{g}})$ europium orbitals (d_{xy}, d_{yz} or d_{zx}) at the $\boldsymbol{R}$th lattice site, and $\mathcal{N}$ is the number of lattice sites inside the Born–von Karmán volume. In the Voigt geometry, when the magnetic field is applied perpendicular to the direction of light travel, the absorption coefficient at a photon energy of $\hbar\omega$ will be given by

$$\alpha^{\parallel,\perp}(\hbar\omega) = \frac{N\pi \mathrm{e}^2 \hbar\omega}{2c\epsilon_0\hbar} \sum_{J=0}^{6} \sum_{M_J=-J}^{+J} \sum_{X} \overline{\left|\mu^{\parallel,\perp}(J, M_J, X)\right|^2} \times g(E_{\mathrm{G}} + E_J - \hbar\omega), \tag{2}$$

where the symbol '$\parallel$' ('$\perp$') denotes the absorption coefficient for light linearly polarized parallel (perpendicular) to the magnetic field direction. Here $g(E)$ is a normalized distribution function that is proportional to the density of states of the $5\mathrm{d}(\mathrm{t}_{2\mathrm{g}})$ conduction band, and whose width at half-maximum is the energy width of the $5\mathrm{d}(\mathrm{t}_{2\mathrm{g}})$ conduction band. E_{G} is the energy bandgap for EuTe, which is magnetic field dependent because of the d–f exchange interaction [10], and E_J represents the Landé split energies of the sextet $4\mathrm{f}^6(^7\mathrm{F}_J)$ europium core. The bar in equation (2) represents an average over all possible spin distributions in the sample, which were obtained at each magnetic field using the molecular field theory, as described in detail in [7].

As shown in [8], in the Faraday geometry, when the light wavevector and magnetic field vector are parallel to one another, the electronic transitions are characterized by electric dipole matrix elements $\mu^{\pm}(J, M_J, X)$, where the plus (minus) sign denotes right (left) circularly polarized light. Similarly, in the Voigt geometry the dipole matrix element that characterizes each possible electronic transition is given by

$$\mu^{\parallel,\perp}(J, M_J, X) = \left[{}^7F M_L = (M_J - 3) M_S = 3 \mid J M_J\right] \times \sum_{m_1=-3}^{m_1=+3} D^{(3)*}_{-M_J+3,m_1}(\alpha_S, \beta_S, \gamma_S) \times \sum_{m'=-2}^{m'=+2} B(X, m') \sum_{m_2=-2}^{m_2=+2} D^{(2)}_{m'm_2}(\alpha_{\mathrm{c}}, \beta_{\mathrm{c}}, \gamma_{\mathrm{c}}) \mathcal{M}^{\parallel,\perp}_{m_1 m_2}, \tag{3}$$

where the symbol '$\parallel$' ('$\perp$') is used to indicate that the incident is linearly polarized parallel (perpendicular) to the magnetic field direction. The multiplying factor $(LM_L SM_S | JM_J)$ is a Clebsch–Gordan coefficient used to expand the $^7\mathrm{F}_J$ state; the coefficients $B(X, m')$ are given by the expansion $|5\mathrm{d}(\mathrm{t}_{2\mathrm{g}})\rangle = |X\rangle = \sum_{m'=-2}^{+2} B(X, m')|5dm'\rangle$, i.e., they determine the $\mathrm{t}_{2\mathrm{g}}$ symmetry orbitals in terms of atomic functions in which the quantization axis is along the [001] crystalline direction.

$D^{(3)}(\alpha_S, \beta_S, \gamma_S)$ and $D^{(2)}(\alpha_c, \beta_c, \gamma_c)$ are Wigner functions required to bring the $|4fm\rangle$ and $|5dm\rangle$ atomic functions, respectively, into the reference frame in which the photon travels along the z-direction (see [8] for more details). The matrix element $\mathcal{M}^{\parallel,\perp}_{m_1m_2}$ is given by $\mathcal{M}^{\parallel,\perp}_{m_1m_2} = \langle 4fm_1|\hat{\xi}^{\parallel,\perp} \cdot \boldsymbol{r}|5dm_2\rangle$, where $\hat{\xi}^{\parallel,\perp}$ is the photon polarization vector and $\boldsymbol{r}$ is the electron's coordinate in the photon's reference frame. For light polarization parallel to the magnetic field direction the result is

$$\mathcal{M}^{\parallel}_{pq} = \frac{\mathrm{i}}{\sqrt{2}} r_{df} \times \begin{array}{c|ccccc} p \backslash q & +2 & +1 & 0 & -1 & -2 \\ \hline +3 & \sqrt{\frac{6}{7}} & 0 & 0 & 0 & 0 \\ +2 & 0 & \frac{2}{\sqrt{7}} & 0 & 0 & 0 \\ +1 & -\sqrt{\frac{2}{35}} & 0 & \sqrt{\frac{12}{35}} & 0 & 0 \\ 0 & 0 & -\sqrt{\frac{6}{35}} & 0 & \sqrt{\frac{6}{35}} & 0 \\ -1 & 0 & 0 & -\sqrt{\frac{12}{35}} & 0 & \sqrt{\frac{2}{35}} \\ -2 & 0 & 0 & 0 & -\sqrt{\frac{2}{7}} & 0 \\ -3 & 0 & 0 & 0 & 0 & -\sqrt{\frac{6}{7}} \end{array}, \tag{4}$$

where $r_{df} \sim 18$ Å is a characteristic length parameter that determines the oscillator strength for the $4f^7 \rightarrow 5d(t_{2g})$ electronic transition [6].

For light polarization perpendicular to the magnetic field direction the matrix $\mathcal{M}^{\perp}$ will be given by

$$\mathcal{M}^{\perp}_{pq} = \frac{1}{\sqrt{2}} r_{df} \begin{array}{c|ccccc} p \backslash q & +2 & +1 & 0 & -1 & -2 \\ \hline +3 & \sqrt{\frac{6}{7}} & 0 & 0 & 0 & 0 \\ +2 & 0 & \frac{2}{\sqrt{7}} & 0 & 0 & 0 \\ +1 & \sqrt{\frac{2}{35}} & 0 & \sqrt{\frac{12}{35}} & 0 & 0 \\ 0 & 0 & \sqrt{\frac{6}{35}} & 0 & \sqrt{\frac{6}{35}} & 0 \\ -1 & 0 & 0 & \sqrt{\frac{12}{35}} & 0 & \sqrt{\frac{2}{35}} \\ -2 & 0 & 0 & 0 & \sqrt{\frac{2}{7}} & 0 \\ -3 & 0 & 0 & 0 & 0 & \sqrt{\frac{6}{7}} \end{array}. \tag{5}$$

The matrices $\mathcal{M}^{\parallel,\perp}$ which characterize the oscillator strength for electric dipole transitions in the Voigt geometry are related to the same matrices $\mathcal{M}^{\pm}$ for Faraday geometry, through

$$\mathcal{M}^{\parallel} = \frac{\mathcal{M}^{+} + \mathcal{M}^{-}}{\sqrt{2}}, \qquad \mathcal{M}^{\perp} = \frac{\mathcal{M}^{+} - \mathcal{M}^{-}}{\mathrm{i}\sqrt{2}} \tag{6}$$

where $\mathcal{M}^{\pm}$ is given in [8].

3. Results and discussion

The MLD spectra were calculated assuming light to travel in the [111] direction. The direction of light travel was chosen because crystals of high crystalline quality are available with their faces lying in (111) planes [6]. For the Voigt geometry the magnetic field, B, must be applied in a direction perpendicular to the direction of the light wavevector, and for simplicity B was chosen along the $[11\bar{2}]$ direction. All material parameters used in the calculations were taken from [7].

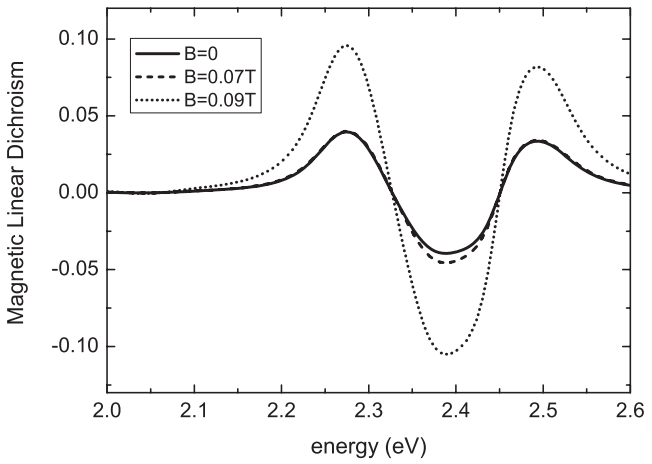

Figure 1. Calculated magnetic linear dichroism for EuTe at $B = 0$, $B = 0.07$ T (slightly below the spin-flop transition), and $B = 0.09$ T (slightly above the spin-flop transition).

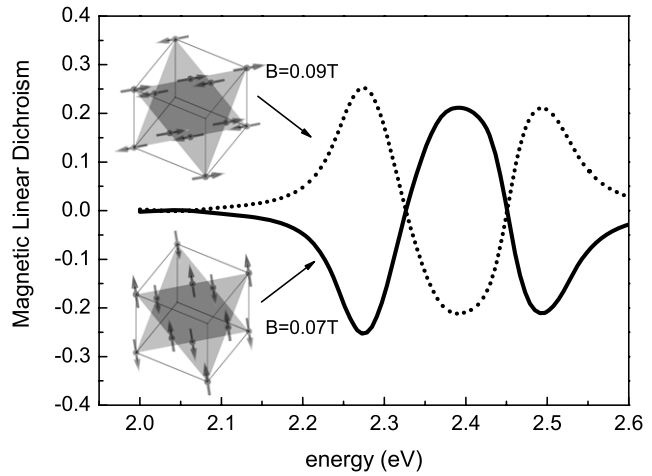

Figure 2. Calculated contribution to the MLD spectrum of a singled out domain. The orientation of the Eu^{2+} spins below and above the spin-flop transition is indicated in the insets. At $B = 0$ the spins point along $[11\bar{2}]$. When a magnetic field is applied along the easy axis, $[11\bar{2}]$, a spin-flop transition occurs at $B \sim 0.08$ T, and the spins flop into the $[1\bar{1}0]$ direction as shown.

Figure 1 shows the calculated MLD spectrum at $B = 0$, $B = 0.07$ and $B = 0.09$ T (below and above the spin-flop transition). At $B = 0$, the MLD signal is smaller than 3% at all energies. When the magnetic field is increased from 0 to 0.07 T, the MLD spectrum remains effectively unchanged. However, when the field is further increased by only 0.02, to 0.09 T, and therefore the spin-flop transition field (0.08 T) is crossed, the MLD signal increases sharply to about 10%. This result is due to the sudden rearrangement of the spin sublattices at the spin-flop transition.

To better understand how a sudden change in MLD can be produced, the contribution to the MLD of a singled out

domain was calculated; this is illustrated in figure 2. The domain chosen is the one for which the applied magnetic field is pointing along its easy axis: as shown in the lower inset of figure 2, at $B = 0$ the spins in this domain lie in the (111) plane and point in the $[11\bar{2}]$ direction, which is also the direction of polarization of one of the incident light rays, $\hat{\xi}^{\parallel}$. At $B = 0.08$ T, the spins flop to the $[1\bar{1}0]$ direction, that is, they become oriented perpendicular to the magnetic field; therefore they become oriented along the direction of polarization of the second light ray, $\hat{\xi}^{\perp}$. The spin arrangement in this domain just above the spin-flop transition is shown in the upper inset in figure 2. Because MLD is a measure of the difference in electronic charge distribution of the two possible directions of polarization of the incident light, $\hat{\xi}^{\parallel}$ and $\hat{\xi}^{\perp}$, and the charge distribution along these two directions is exchanged at the spin-flop transition, the MLD signal from this isolated domain reverses sign at the spin-flop transition. Notice also that both below and above the spin-flop transition the spins are arranged antiferromagnetically; thus the MCD signal remains zero at all times, both below and just above the spin-flop transition.

However, in an experiment in which light is made to pass through the sample, all spin domains present in the sample will be probed, and not a single domain as illustrated in figure 2. Therefore a realistic MLD signal must be calculated using (2) where α denotes the absorption coefficient averaged over all domains [7]. The results of the calculation averaged over all possible configurations is depicted in figure 1, and it shows that MLD is nearly zero below the spin-flop transition field ($B_{\rm sf}$), and displays a step-like increase when the spin-flop field is crossed. The step-like increase of the MLD signal at the spin-flop field can be understood as follows. At $B = 0$, twelve different antiferromagnetic domains are present in the material [9], composing an ensemble of spins that are oriented in all directions almost homogeneously, and therefore characterized by a very small linear dichroism. Above the spin-flop transition, the molecular field model [7] shows that there is a tendency for the spins to become oriented mostly perpendicular to B (i.e. along $[11\bar{2}]$). Therefore, when the spin-flop transition occurs, the electronic charge distributions along the magnetic field direction, $\hat{\xi}^{\parallel}$, and along a direction perpendicular to it, $\hat{\xi}^{\perp}$, become very different; consequently MLD becomes larger in comparison to its value at $B = 0$.

The evolution of MLD as a function of applied magnetic field is shown in figure 3, in which the sudden increase in MLD at the spin-flop transition can be distinguished. On increasing the magnetic field above the spin-flop transition field, MLD gradually decreases and it approaches zero at $B \sim 5.2$ T. For magnetic fields larger than 5.2 T MLD increases again, however, with a reversed sign, and at the saturation field, $B_{\rm sat} = 7.2$ T [10], which characterizes full ferromagnetic arrangement, MLD reaches maximum values and is unchanged for larger fields. The redshift of the spectrum at high fields, seen in figure 3, is due to the d–f exchange interaction between electrons in the $5d(t_{2g})$ extended states and localized $4f^7(^8S_{7/2})$ spins [10, 11], which shortens the bandgap.

The MLD sign reversal at high fields relative to the low field situation can be understood from the fact that just above the spin-flop transition there is predominant tendency

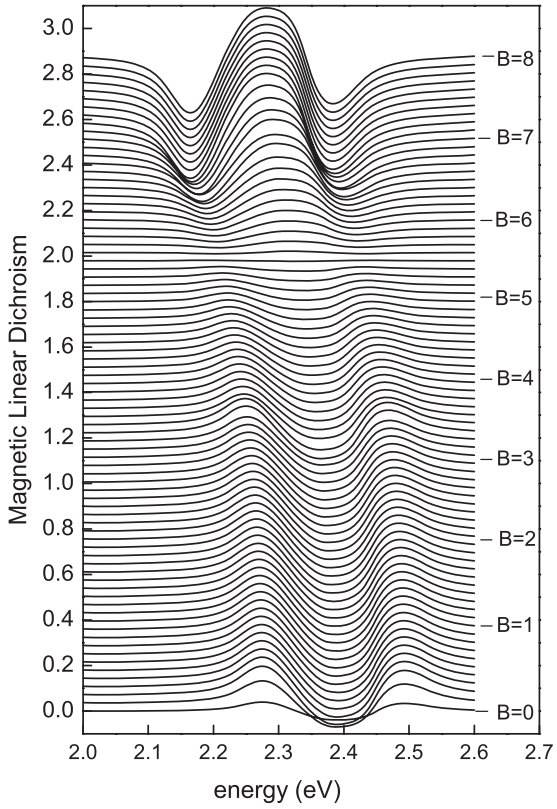

Figure 3. Evolution of the calculated MLD spectrum as a function of the applied magnetic field.

for the spins to lie in a plane perpendicular to B, whereas at high fields when saturation is reached the spins are aligned with B. Therefore the roles of $\alpha^{\parallel}$ and $\alpha^{\perp}$ are reversed, leading to a change of sign in MLD (a simple illustration of this effect, for a single domain, is shown in figure 2 and discussed above). The larger absolute value of MLD at high fields in comparison to its value just above the spin-flop transition is due to the fact that above the spin-flop transition the sample still contains several spin domains, which contain spins oriented in different direction, and therefore their contributions to MLD can partially cancel each other, whereas at the saturation field a single spin orientation is allowed. Finally, it is observed that at about $B \sim 5.2$ T MLD is approximately zero. This is an indication that at this field the average electronic charge distribution in the $\hat{\xi}^{\parallel}$ and $\hat{\xi}^{\perp}$ directions becomes nearly identical, which is a consequence of the gradual tilting of the spins towards the magnetic field direction when B increases.

4. Conclusion

In conclusion, we have used the extended $4f^7(^8S_{7/2}) \rightarrow 4f^6(^7F_J)5d(t_{2g})$ model, which takes into account the spin domain structure, to calculate the magnetic linear dichroism in EuTe. It was shown that MLD can be very sensitive to the distribution of spin orientations in the sample. In particular, MLD shows a step-like increase at the spin-flop transition. Above the spin-flop transition, MLD slowly decreases and

it becomes zero when the averaged electronic charge of the $4f^7(^8S_{7/2})$ becomes symmetric with respect to the direction of the light wavevector. Further increase of the magnetic field favours further alignment of the spins with the magnetic field direction, and MLD changes sign. At the saturation magnetic field intensity full ferromagnetic alignment of the spins is reached, and MLD reaches the maximum values of ∼0.3. Therefore MLD measurements could be used as a sensitive probe of the spin order, and could provide information that is not accessible through the magnetic circular dichroism spectra.

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