

Chapter 2

The magneto-optical spectrum of EuO

Until recently, most of what was known about the electronic structure of EuO was based on optical measurements and band structure calculations. The interpretation of the optical and magneto-optical spectra has appeared to be rather difficult and several contradictory explanations of these spectra have been given. Before we will discuss measurements of the electronic structure using new spectroscopic methods in the next chapters, we will discuss how we can understand the optical properties.

2.1 Spectrum of Eu²⁺ ion

From band structure calculations [142] and early photoemission studies [83–86] it was found that the highest valence band orbitals of EuO are the Eu 4*f* orbitals. Calculations [56, 142] also show that the conduction band is formed mainly by Eu 5*d*. Therefore the lowest energy interband transitions in EuO are from the Eu 4*f* orbitals to the Eu 5*d* conduction band. Before we treat the optical spectrum of EuO let us first consider the energies of these transitions in a Eu²⁺ atom. Hund's first rule tells us that the lowest energy state of the Eu 4*f*⁷ atom will have a maximum spin of $S = 7/2$. As the exchange interactions between 4*f* electrons are large, the ground state will thus have a very pure ⁸*S* character, with $L = 0$ (and thus $l_z = \sum m_l = 0$), $S = 7/2$ and $J = 7/2$. The excited states have a Eu 4*f*⁶5*d*¹ configuration. As transitions from an $L = 0$ initial state to an $L = 0$ final state are not allowed (parity has to change), $\Delta L = +1$ and in Russel-Saunders coupling the final state has $L = 1$, $S = 7/2$ and thus $J = |S - L| \dots S + L = \frac{5}{2}, \frac{7}{2}, \frac{9}{2}$. In the presence of spin-orbit coupling, spin and orbital angular momentum mix and the final states $J = 7/2$ and $J = 5/2$ now also have some $S = 5/2$ character, with the spin of the 5*d* electron directed opposite to that of the 4*f* electrons. As a result of the less favorable spin-configuration these 2 'spin-flip' final states will have a higher energy. Therefore we expect 5 different final state energies. In the excitation spectrum of free Eu²⁺ ions

Sugar and Spector [143] found 6 strong peaks (intensity > 100), one of which they attributed to a $J = 9/2$ final state, two were assigned to a $J = 7/2$ final state and three to the $J = 5/2$ final state, corresponding to the optical selection rule $\Delta J = 0, \pm 1$. Two of the three $J = 5/2$ final states are separated only by 132 cm^{-1} and therefore probably correspond to the same type of transition. The number of main peaks is thus nicely consistent with the 5 transitions expected from optical selection rules.

2.2 Europium atoms in crystals

When a europium atom is incorporated in a lattice its optical spectrum is strongly modified as a result of the crystal field. The effect of the crystal field on the $4f$ electrons is however much smaller than that on the $5d$ electrons. Therefore the $4f$ electrons should be treated [32] by a weak crystal field with

exchange splittings $>$ spin-orbit coupling $>$ crystal fields.

And the $5d$ electrons are subjected to a strong crystal field with

crystal field $>$ exchange splitting $>$ spin-orbit coupling.

Therefore the final state energy will be mainly determined by the crystal field splitting of the $5d$ electron and by the total angular momentum J_{4f} of the 6 remaining $4f$ electrons. Additionally the exchange interaction between the $5d$ electron and the $4f$ electron can change the final state energy. However as spin-flip transitions are only weakly allowed via spin-orbit coupling, these spin-flip final states will only slightly affect the absorption spectrum. From this evaluation we therefore expect the optical spectrum of Eu ions in a lattice to consist of 2 peaks corresponding to the e_g and t_{2g} final states each of which is split into a septet corresponding to the $J = 0 \dots 6$ states of the $4f^6$ configurations. Such structures were convincingly found in the optical spectra of EuF_2 and of Eu doped SrS and KBr by Freiser *et al.* [67, 144] as is shown in figure 2.1. It should be noted that EuF_2 has a fluorite structure and as a result of the crystal field the e_g orbitals have the lowest energy. The other compounds have a rocksalt structure with Eu t_{2g} as the lowest unoccupied states. The authors interpreted the data along the same lines as we described above. In a later work, Kasuya [7] arrived at similar conclusions, with the multiplet structure arising as a result of different $J_{4f} = 0 \dots 6$. In the europium chalcogenides the sharp multiplet structures were generally not observed, instead a broad peak with a width of around 0.7 eV is usually found. Possibly the $4f$ multiplets are smeared out in the chalcogenides as a result of $5d$ band formation. It is however also possible that the optical spectra are blurred by surface oxidation of the reactive materials. In fact in situ reflectivity measurements by Güntherodt [75] on polished EuS crystals showed very similar multiplet structures in the imaginary part of the dielectric function indicating that the europium chalcogenides should be interpreted similarly to EuF_2 .

In the work by Kasuya the $4f^6 5d^1$ energy levels were labelled by values $J_{\text{Kasuya}} \equiv S + L_{4f}$ where L_{4f} was the orbital angular momentum of the $4f$ electrons. This

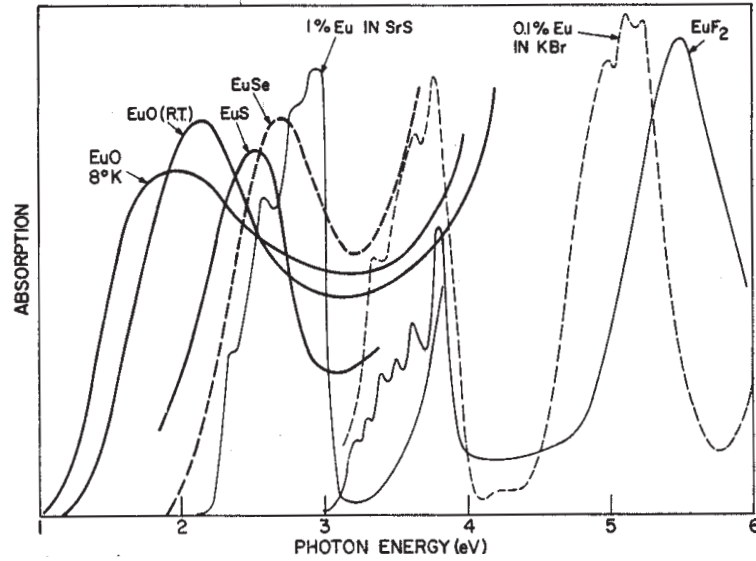


Figure 2.1: Absorption spectra of several materials containing Eu^{2+} ions. From [67].

labelling was rather unfortunate as it was interpreted by Schoenes and coworkers [8, 81, 137, 145, 146] that the atomic optical selection rules for J could be applied to Kasuya's J , with only the final states with $J_{\text{Kasuya}} = \frac{5}{2}, \frac{7}{2}, \frac{9}{2}$ being optically allowed. The application of the optical selection rules to J_{Kasuya} is however incorrect as the orbital angular momentum L_{5d} of the $5d$ electron is neglected in the process.

2.3 Transition probabilities

The magneto-optical spectra in EuO is mainly different from spectra of other compounds containing Eu^{2+} ions due to interactions of the excited $5d$ electron with its surroundings. Such interactions can result in the formation of a Eu $5d$ band and increase the $5d$ exchange splitting in the ferromagnetic phase. However the main features that determine the magneto-optical spectrum in these compounds are still the $4f^6$ multiplets in the final state. As the $4f$ shell is rather insensitive to its surroundings, these effects will be similar for all compounds containing Eu^{2+} and their spectra should thus be explained along similar lines. Numerous studies [7, 145, 147–154] have addressed the subject of the optical absorption spectrum of Eu^{2+} . A very good agreement between calculated and measured spectra of Eu^{2+} impurities was found by Weakliem [147] who diagonalized the full 196×196 matrix of $f^6(^7F_J)5d^1(e_g)$ final states, including spin-orbit and $f-d$ Coulomb interactions. He found that a best fit with the experimental $\text{Eu}^{2+}:\text{CaF}_2$ data was obtained by taking the $f-d$ exchange integral $G_1=14$ meV and a $5d$ spin-orbit coupling of 31 meV. The smallness of these parameters suggests that the effects of $5d-4f$ exchange and

5d spin-orbit coupling on the magneto-optical spectrum are weak. This motivated us to calculate the magneto-optical spectrum in a simpler approximation, neglecting these effects. Although the results are less generally valid, we present them here as they provide a simpler insight in the essentials that determine the magneto-optical spectrum.

2.3.1 Calculations

The calculation is performed assuming that the angular part of the 4f and 5d orbitals are still well approximated by hydrogenic wave functions. In the initial state the 4f shell contains seven electrons with $m_l = -l \dots l$ and $l = 3$ (effects of crystal field splitting on the 4f orbitals are neglected). After optical absorption, one of these electrons is excited to the 5d band and is thus in an e_g or t_{2g} orbital with $l = 2$. The optical dipole transition rate $R_{i \rightarrow f}$ is given [155] by:

$$R_{i \rightarrow f} \propto |\langle \phi_f | \varepsilon \cdot \mathbf{r} | \phi_i \rangle|^2 \quad (2.1)$$

where $\varepsilon = (\varepsilon_x, \varepsilon_y, \varepsilon_z)$ is the polarization vector of the light. As the radial integrals are the same for all 4f – 5d transitions, the transition rates only depend on the angular components and can be expressed as integrals of the spherical harmonics Y_{l,m_l} as follows:

$$\begin{aligned} \langle \phi_f | \varepsilon \cdot \mathbf{r} | \phi_i \rangle &\propto \int d\Omega \phi_f^*(\theta, \phi) \varepsilon \cdot \hat{\mathbf{r}} Y_{3,l_{zi}}(\theta, \phi) \\ \varepsilon \cdot \hat{\mathbf{r}} &= \sqrt{\frac{4\pi}{3}} \left(\varepsilon_z Y_{1,0} + \frac{-\varepsilon_x + i\varepsilon_y}{\sqrt{2}} Y_{1,1} + \frac{\varepsilon_x + i\varepsilon_y}{\sqrt{2}} Y_{1,-1} \right) \end{aligned} \quad (2.2)$$

The angular parts of the t_{2g} and e_g final states ϕ_f are [32, 156]:

$$\begin{aligned} &\phi_{t_{2g}} \\ &xy : (-iY_{2,2} + iY_{2,-2}) / \sqrt{2} \\ &xz : (-Y_{2,1} + Y_{2,-1}) / \sqrt{2} \\ &,yz : (iY_{2,1} + iY_{2,-1}) / \sqrt{2} \\ &\phi_{e_g} \\ &x^2 - y^2 : (Y_{2,2} + Y_{2,-2}) / \sqrt{2} \\ &3z^2 - r^2 : Y_{2,0} \end{aligned} \quad (2.3)$$

We choose the quantization axis (z -axis) parallel to the atom's magnetization in the initial ${}^8S_{7/2}$ ground state, i.e. such that $j_z = \frac{7}{2}$. Using equations (2.1), (2.2) and (2.3) we have calculated the transitions rates $R_{m_l, t_{2g}} = \sum_{t_{2g}} R_{\phi_{4f, m_l} \rightarrow \phi_{t_{2g}}}$ and $R_{m_l, e_g} = \sum_{e_g} R_{\phi_{4f, m_l} \rightarrow \phi_{e_g}}$ for different polarization vectors with respect to the quantization axis. The integrals were analytically evaluated for linear polarized light parallel

m_l	$R_{m_l, t_{2g}} \times 420$					$R_{m_l, e_g} \times 420$					$j_{z, 4f}$
	ε_{\perp}	ε_{\parallel}	ε_+	ε_-	ε_{avg}	ε_{\perp}	ε_{\parallel}	ε_+	ε_-	ε_{avg}	
3	45	0	0	90	30	45	0	0	90	30	0
2	60	30	0	120	50	0	30	0	0	10	1
1	3	96	6	0	34	39	0	6	72	26	2
0	36	0	36	36	24	0	108	0	0	36	3
-1	3	96	0	6	34	39	0	72	6	26	4
-2	60	30	120	0	50	0	30	0	0	10	5
-3	45	0	90	0	30	45	0	90	0	30	6

Table 2.1: Transition rates with certain $j_{z, 4f}$.

J_{4f}	$R_{J_{4f}, t_{2g}} \times 44100$					$R_{J_{4f}, e_g} \times 44100$				
	ε_{\perp}	ε_{\parallel}	ε_+	ε_-	ε_{avg}	ε_{\perp}	ε_{\parallel}	ε_+	ε_-	ε_{avg}
0	675	0	0	1350	450	675	0	0	1350	450
1	1725	525	0	3450	1325	675	525	0	1350	625
2	1788	2541	126	3450	2039	1494	525	126	2862	1171
3	2733	2541	1071	4395	2669	1494	3360	126	2862	2116
4	2838	5901	1071	4605	3859	2859	3360	2646	3072	3026
5	5988	7476	7371	4605	6484	2859	4935	2646	3072	3551
6	10713	7476	16821	4605	9634	7584	4935	12096	3072	6701

Table 2.2: Transition rates to states with certain J_{4f} .

(ε_{\parallel}) and perpendicular (ε_{\perp}) to the quantization axis, for left and right-circularly polarized light (ε_{\pm} , $\Delta m_l = \pm 1$, with $\varepsilon \perp z$) and for an angular average over all light polarizations (ε_{avg}). The results are shown in table 2.1.

The $4f$ -shell has $s_{z, 4f} = 7/2$ in the initial state, one electron is removed and thus in the final state $s_{z, 4f} = 3$. In the initial state $l_{z, 4f} = \sum m_{l, 4f} = 0$, removing one electron with orbital angular momentum m_l thus leads to $l_{z, 4f} = -m_l$ in the final state, therefore $j_{z, 4f} = s_{z, 4f} + l_{z, 4f} = 3 - m_l$ as indicated in table 2.1. As the 3 t_{2g} orbitals are essentially degenerate just like the 2 e_g orbitals, the final state energy is mainly determined by the crystal field splitting and the total angular momentum J_{4f} of the remaining $4f$ electrons. As there are $2J_{4f} + 1$ state functions ϕ_{J_{4f}, j_z} with $j_z = -J_{4f} \dots J_{4f}$, each of the final states with a specific j_z is a superposition

$$\phi_{j_z} = \frac{1}{\sqrt{7 - |j_z|}} \sum_{J_{4f} \geq |j_z|}^6 \phi_{J_{4f}, j_z} \quad (2.4)$$

Therefore the transition rate to a final state with a specific J_{4f} is

$$R_{J_{4f}} \propto \sum_{|j_z| \leq J_{4f}} \frac{R_{j_z}}{7 - |j_z|} \quad (2.5)$$

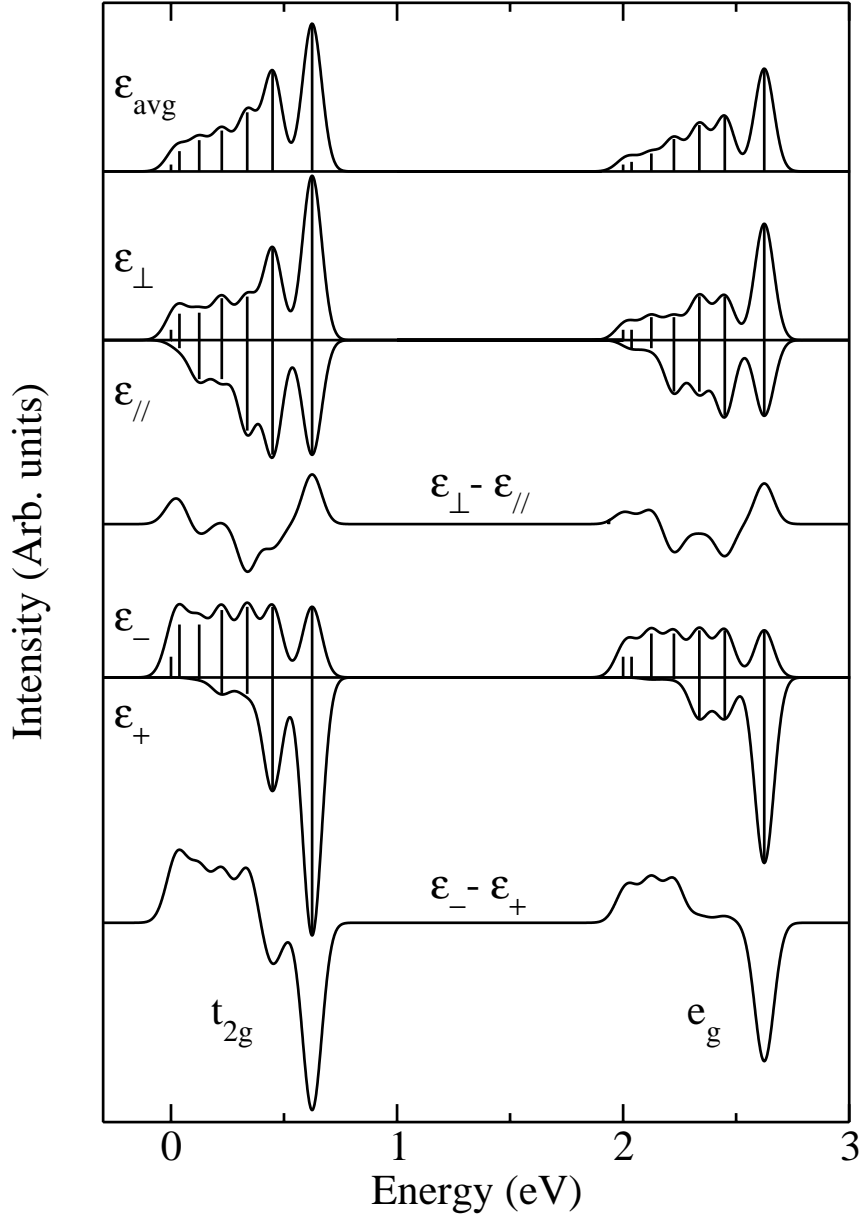


Figure 2.2: Calculated $Eu^{2+} 4f \rightarrow 5d$ spectra for linearly polarized light perpendicular (ϵ_{\perp}) and parallel (ϵ_{\parallel}) to the z -axis, left and right-circular polarized light (ϵ_{\pm}) and unpolarized light (ϵ_{avg}). Also shown are the magnetic linear ($\epsilon_{\perp} - \epsilon_{\parallel}$) and circular ($\epsilon_{-} - \epsilon_{+}$) dichroism spectra. The z -axis is taken such that $j_{z,4f} = \frac{7}{2}$ in the initial state.

2.3.2 Comparison with Eu^{2+} impurities

Thus we find the transition probabilities to the different J final states as tabulated in table 2.2. In figure 2.2 we show the resulting calculated spectra, making use of the

experimentally obtained energy splittings [144] between the different J multiplets and a crystal field splitting $10D_q$ of 2 eV. Gaussian broadened spectra are also shown. The absorption intensity distribution of the calculated multiplets is similar to that measured in EuF_2 (figure 2.1). Large spectral changes occur when the polarization of the light is changed. In fact at the bottom of the absorption edge, the absorption of circularly polarized light is 100% helicity polarized, i.e. $(\alpha_{\varepsilon_-} - \alpha_{\varepsilon_+})/(\alpha_{\varepsilon_-} + \alpha_{\varepsilon_+}) = 1$. The calculation shows how the $4f \rightarrow 5d$ transitions from the 8S ground state can account for the very large magneto-optical effects in compounds containing Eu^{2+} ions, effects which are among the strongest known for any class of compounds [151, 157–159]. The obtained spectra are indeed similar to the more sophisticated calculations by Weakliem [147] and account very well for the observed magneto-optical spectra of $\text{Eu}^{2+}:\text{CaF}_2$ and $\text{Eu}^{2+}:\text{KCl}$ like in figure 2.3 [147, 154].

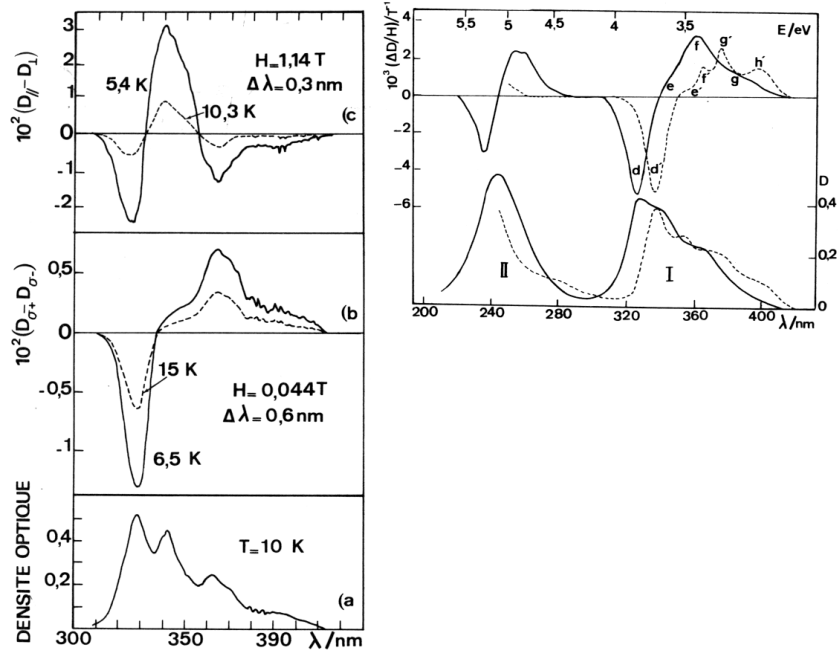


Figure 2.3: Optical absorption and MCD and MLD at $5d_{t_{2g}}$ in $\text{Eu}^{2+}:\text{KCl}$ at 10 K (left) and MCD of $\text{Eu}^{2+}:\text{CaF}_2$ at room temperature (right), reproduced from Ferré *et al.* [153, 154]. Note that $D_{\sigma_{\pm}}$ corresponds to ε_{\mp} and $D_{\parallel, \perp}$ to $\varepsilon_{\parallel, \perp}$.

2.3.3 Comparison with europium chalcogenides

Although the model reproduces the multiplets in the spectra of EuF_2 and of compounds containing Eu^{2+} impurities very well, the absorption spectra of the Eu chalcogenides are much broader. Possibly this is due to band formation. To model such band formation, we have convoluted the $5d$ density of states as obtained by LDA+U

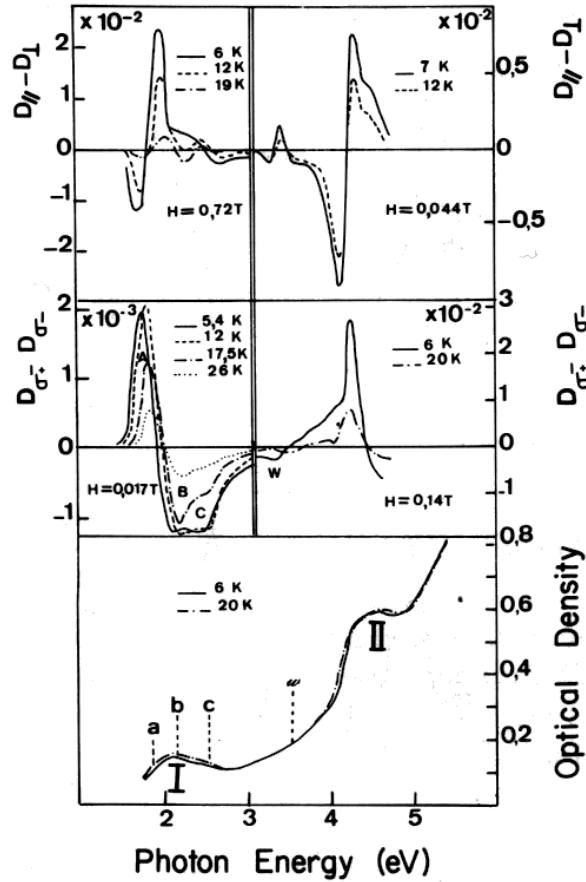


Figure 2.4: Optical absorption, MCD and MLD of thin film of EuS deposited onto CaF_2 , reproduced from Ferré *et al.* [153, 154]. Note that $D_{\sigma\pm}$ corresponds to ε_{\mp} and $D_{\parallel,\perp}$ to $\varepsilon_{\parallel,\perp}$.

of EuO (see [56] and figure 4.5), with the calculated multiplet structures. The resulting spectra have absorption peak energies of $\sim 3\text{-}4$ eV and do not reproduce the measured absorption spectrum of EuO, which peaks around 2 eV. This indicates that excitonic effects pull spectral weight towards the band bottom as was suggested by Kasuya [4]. Recently an attempt was made to model the magneto-optical properties of EuO using an energy-band theory [160], which resulted in a too broad theoretical spectrum, possibly as a result of the same excitonic effects, which tend to reduce the effect of band formation on the broadening of the energy levels. This excitonic effect also explains why the ionic approximation, in which we calculated the magneto-optical spectrum of Eu^{2+} , still provides a reasonable description of the measured magneto-optical spectrum in the chalcogenides [77, 137, 145, 153] as can be seen by comparing figures 2.4 and 2.2.

From the calculated spectra we can also understand why the shift of the ab-

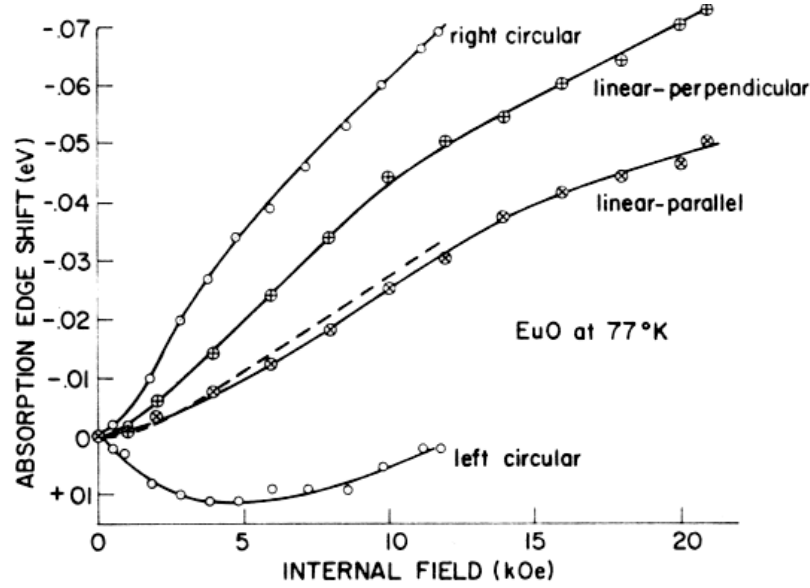


Figure 2.5: Absorption edge shift of EuO at 77 K for different magnetization directions and light polarizations as function of the internal magnetic field, reproduced from Freiser *et al.* [67].

sorption edge strongly depends on the polarization of the light when the sample is magnetized. In figure 2.5 we reproduce data by Freiser *et al.* taken at 77 K. Besides a shift of the absorption edge as a result of the exchange splitting of the conduction band with increasing magnetization, magnetic dichroism also results in a shift of the absorption edge. The effect of dichroism on the shift can be understood by comparing figures 2.2 and 2.5. When no internal magnetic field is present, the Eu spins will be randomly oriented and the optical spectrum will be similar to that of ε_{avg} . Upon application of a field the Eu moments will align with the magnetization and the absorption edge will shift as a result of the exchange splitting, as will be discussed in more detail in chapter 5. Additionally a shift of the absorption edge is induced by dichroism. As the absorption spectrum in figure 2.2 for ε_{\perp} is the most similar to that for ε_{avg} , the smallest dichroic contribution is expected for a light polarization vector ε_{\perp} . For ε_{\parallel} a small shift of the bottom edge of the conduction band to higher energies is expected while for ε_{+} the dichroic shift of this edge to higher energies even exceeds the reduction due to exchange splitting. For right-circular polarized light (ε_{-}) the shift of the absorption edge is increased by dichroism as observed.

The calculated spectra contradict the claim of Freiser *et al.* [67] that the spectra with the polarization vector parallel to the magnetization (ε_{\parallel}) are free of dichroism. This is an important observation as it means that to measure the temperature dependence of the absorption edge as a result of the exchange splitting, the configuration with the magnetic field parallel to the light polarization is not optimal as it might introduce a small reduction of the shift due to dichroic effects (Freiser *et*

al. use a field $H_{\parallel} = 2$ kOe). Instead measurements with zero total magnetization would be preferable, as ε_{avg} would be measured at all temperatures.

2.4 Conclusions

We have analytically calculated the magneto-optical spectrum of $4f \rightarrow 5d$ transitions on Eu^{2+} ions using several simplifying approximations. The calculated spectra agree very well to the measured spectra of Eu^{2+} impurities in crystals and also agree well to more sophisticated calculations. Thus we have shown that the multiplet structures and large magneto-optical effects in these compounds are essentially a result of the polarization dependent transition rates to different J_{4f} final states when exciting a $4f$ electron to the $5d$ band. We argue that the magneto-optical effects in the Eu chalcogenides have the same origin. Moreover we showed that the polarization dependence of the shift of the absorption edge can be well understood from the calculated dichroic effects.