Doctoral Thesis

Magneto-optical Kerr-effect of uranium-compounds
a study of the electronic and magnetic structure

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MAGNETO-OPTICAL KERR-EFFECT OF URANIUM-COMPOUNDS: 
A STUDY OF THE ELECTRONIC AND MAGNETIC STRUCTURE

A dissertation submitted to the 
SWISS FEDERAL INSTITUTE OF TECHNOLOGY ZUERICH

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Doctor of Natural Sciences

presented by

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1984
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ABSTRACT

A comprehensive study of the magneto-optical properties of metallic uranium compounds is presented in the 0.5 - 6 eV photon energy range. New results about the electronic and the magnetic structure of these materials are derived.

The f states are best described in an itinerant model with an occupation of nearly 3 for all investigated materials except the Th$_3$P$_4$-structure compounds, although correlation effects are shown to play a dominant role in UTe. A spin-polarized band structure of f and d states in the system UTe-Usb-YSb is derived and the competition of f-d and f-p hybridization in this system is discussed. The maintenance of a $f^3$-$f^2$ valence transition in the Usb-YSb pseudo-binary system is challenged.

The magnetic f-d exchange energy is established to be negative for all investigated materials i.e. the f and d moments align antiparallel upon magnetic ordering. This property manifests itself in two magneto-optical effects: First, the conduction electron spin-polarization displays a negative sign and its size is observed to range up to -100% for certain compounds, which is an extraordinary value for magnetic metals. Second, the f+d transition energy displays a magnetic red-shift in the order of 200meV due to the formation of spin-polarized subbands of the d states which are energetically split by the exchange energy. The size of the magnetic shift is found to depend on the sublattice magnetization rather than on the net moment which results in similar magnitudes for some ferro- and antiferromagnets. This behavior completely differs from the one known up to now for antiferromagnetic semiconductors, but is well understood in terms of the magnetic structure of the uranium pnictides.

For most of the materials, the value of the f polarization is calculated. The f moment itself is evidenced to consist of antiparallel spin and orbital contributions with a predominant orbital part in most of the investigated NaCl-structure compounds.

Some of the investigated uranium systems seem to be very promising candidates for technical applications due to the by far largest Kerr-rotation ever observed for metals, reaching up to $9.7^\circ$ at 65% reflectivity.
KURZFASSUNG

In dieser Arbeit wird über eine umfassende Untersuchung der magneto-optischen Eigenschaftenmetallischer Uran-Verbindungen im Energiebereich zwischen 0.5 und 6 eV berichtet. Neue Erkenntnisse sowohl über die elektronische als auch die magnetische Struktur dieser Substanzen, die sich aus der Analyse der magneto-optischen Daten ergeben, werden diskutiert.


Einige der untersuchten Materialien bieten vielversprechende Voraussetzungen für technische Anwendungen, ist doch die maximale beobachtete Kerr-Drehung von $\approx 9.2^\circ$ bei 65% Reflexion um mindestens eine Größenordnung grösser als in allen bekannten nicht-5f Metalen.
1. INTRODUCTION

It is well known, that with a few exceptions only in compounds of 3d, 4f and 5f elements magnetic long range order appears. In most of the 4f systems, the f electrons are localized and form a Hund's rule ground state. The magnetic properties of these materials are in fact well understood in terms of the Heisenberg exchange model. On the other hand, the 3d electrons in most of the metallic transition metal compounds form relatively wide bands with a totally quenched orbital momentum. A qualitative idea about the origin of magnetism in these materials may be obtained in the Stoner picture of exchange-split spin-polarized subbands. However, this description is certainly far from reality because it predicts e.g. for the magnetic susceptibility a wrong temperature dependence. Recent experiments, however, indicate Stoner-like behavior at certain points in the Brillouin-zone but a temperature independent exchange splitting at other symmetry points [1]. A more quantitative description of band magnetism than the Stoner model has been attempted by some sort of 'unified' theory which combines aspects of both the itinerant and localized models [2-5], but a complete theory is still lacking.

In view of this dilemma in theory it appears promising to study magnetic 5f compounds, which are expected to bridge the gap between itinerant and localized behavior of magnetic electrons. In particular, the 5f systems may provide the opportunity of a gradual localization with increasing separation of the magnetic ions.

Yet, an intensive experimental and theoretical study in the last decade [6] has revealed that 5f magnetism is more complex than expected, because Coulomb, spin-orbit, crystalline field and exchange energies are in the same order of magnitude. In addition, for certain compounds strong f-d and f-p hybridization result in a f bandwidth, which is nearly independent of the lattice constant and this hybridization is often the reason for the metallic behavior of these compounds. The intermediate magnetic behavior of certain 5f materials is elucidated by a recent theoretical work [7] which predicts a substantial orbital contribution to the uranium moment for the itinerant antiferromagnet UN. Hence, electronic structure and magnetism are strongly related in these materials and a knowledge of the spin-polarized band structure is desirable.

The bearing of magneto-optics for the study of spin-polarized electrons comes of the proportionality of the polar magneto-optical effects (Fara-
day- and polar Kerr-effect) to the spin-polarization of the involved electronic states. By a combination of optics and magneto-optics these states may therefore be identified and analyzed in respect to their spin-polarization, symmetry character and energy. It is noteworthy to mention in this context, that compared to spin-polarized photoemission experiments, the polar Kerr-effect is known to be much less sensitive to surface effects.

Unfortunately, this experimental potential to study itinerant magnetism could not be applied much to the 3d metals because no dipole allowed optical transitions occur at energies up to 5 eV. In the case of metallic 5f compounds, on the other hand, dipole allowed excitations of f and d electrons are expected at low energies allowing the study of spin-polarized d and f bands a few eV around $E_F$. For the same reasons, a direct determination of magnetic exchange energies may be possible similar to the situation in the Eu-chalcogenides [8,9].

The magneto-optical properties of 5f compounds have not been investigated up to now with the exception of UO$_2$, which is the only cubic 5f magnetic semiconductor based on uranium. It has been shown, that the magneto-optical response of the localized 5f$^2$ ground state of UO$_2$ displays large similarities to the Eu-chalcogenides and that it is governed by a final state splitting of the $f^2 \rightarrow f^1d^1$ transition [10]. The magneto-optical signal can be understood perfectly in terms of atomic theory, treating the $f^1d^1$ final state as a whole. In this work, the complex magneto-optical polar Kerr-effect of various metallic uranium compounds is presented and discussed.

In section 4, the electronic structure of uranium chalcogenides and pnictides will be compared and trends along these series are discussed. For these materials, a direct examination of the magnetic f-d exchange is possible. In section 5, the effect of dilution of the magnetic ion is studied in $U_xY_{1-x}$Sb with special emphasis on the claimed $f^3 \rightarrow f^2$ valence transition [11] in this system. In sections 6 and 7, the f,d ground state of uranium in different crystallographic structures is examined. In section 8 finally, some aspects of the technical application of magneto-optics are discussed in the light of the extraordinary magneto-optical response of the present materials.

During the course of this work, also some intermetallics like UPd$_3$, UPt$_3$ and UIr have been investigated. However, the magneto-optical response even of ferromagnetic UIr was found to be less than 0.05°. Up to now, these compounds have not been studied further.
2. EXPERIMENTAL DETAILS

2.1 Samples

All experiments to be discussed in this work have been performed on single crystals. In general, the crystals have been cleaved in air followed by a quick transfer into the cryostat. Some \( \text{USb}_x\text{Te}_{1-x} \) and \( \text{U}_x\text{Y}_{1-x}\text{Sb} \) crystals have either been cleaved in the argon chamber and were transferred subsequently without contact to air into the cryostat or they have been cleaved in the cryostat in helium atmosphere a few minutes before measurement. We found no differences in the magneto-optical spectra obtained from surfaces prepared by these three methods apart from slight changes of the size of the magneto-optical response by less than 5%. Deviations in the same order of magnitude have been observed between spectra obtained from cleaved crystals with different surface roughness. It is interesting to note, that the magneto-optical response of a cleaved crystal remains nearly unchanged even if the optical reflectivity is reduced by a factor of three due to an imperfect surface. In general it is to state, that the magneto-optical Kerr-effect is very insensitive on surface preparation for the investigated uranium compounds.

In contrast to the cleaved samples, tremendous changes of the spectra have been observed for polished samples. Due to this surface treatment, several effects are found to occur. A first observation is, that the size of \( \theta \) and \( \varepsilon \) deviates at \( \hbar \omega > 3 \text{eV} \) from those spectra obtained for cleaved samples, which is illustrated for US-(100) in fig.1. This effect may have the same reasons as the difference of the reflectivities at high energies for cleaved and polished samples [12].

In the case of \( \text{USb}_0.8\text{Te}_{0.2} \) we have observed a complete change of the magneto-optical \( f\pm d \) transition signal due to polishing. On the one hand, this behavior gives new insight into the physical properties of this special material (discussed in sec. 4.4.2.2) but on the other hand shows, that the measurement of a polished sample can lead to misinterpretations. Finally, the polishing treatment may influence the magnetic structure of the sample. This effect has been observed for UAs [13] and is discussed in detail in sec. 4.5.

The magneto-optical results, presented in the following chapters have therefore been obtained on cleaved samples as far as possible. The inves-
tigation of Th$_3$P$_4$-structure compounds, which are not cleavable, and of course the measurements on (111)- and (110)-oriented surfaces of cubic compounds have been performed on polished samples.

![Graph](image)

**Fig. 1:** Polar Kerr-rotation $\theta_K$ and -ellipticity $\varepsilon_K$ of uranium-mono-sulfide at magnetic saturation ($B=4T$, $T=15K$). a) (100)-cleaved. b) (100)-polished.

### 2.2 Magneto-optical measurements

Fig. 2 shows the principal components of the equipment for the determination of $\theta_K$ and $\varepsilon_K$ in the photon energy range between 0.5 eV and 5.7 eV. To achieve high light intensities $I_0$, we have used a 50W halogen lamp below $\approx 2.5$ eV and a 450W Xenon arc light source above $\approx 2.5$ eV. The light is polarized by an air gap Glan-Thomson polarizer. The sample and the reference mirror are mounted in a gas flow cryostat which allows measurements in the 1.5-300 K temperature range. Magnetic fields up to 10 T are generated by a split coil superconducting magnet. The angle of incidence is kept less than $3^\circ$ to avoid mixing of the polar Kerr-signal with quadratic magneto-optical effects. In fact, a calculation of the Kerr-
Fig. 2: Experimental set-up for the polar Kerr-measurement in the 0.5-5.7 eV photon energy range.

effect as function of the angle of incidence has proved, that the deviation from the result at normal incidence is negligible at such small angles of incidence [14].

The reflected light is modulated by a Faraday modulator, using a SCHOTT SF-59 glass or a quartz rod of 10 cm length for wavelengths below and above 2.5 eV, respectively. With an analyzer setting of 90°±6 relative to the polarizer setting (nearly crossed) and a modulation φ= φ₀ sin ωt, one obtains as a function of the Kerr-rotation θₖ at the detector an intensity of the form

\[
I_0 = \frac{1}{2} \left[ (1 - J_0(2φ₀) \cos(2(θ₁ - δ))) + 2 \sin(2(θ₁ - δ)) J_1(2φ₀) \sin ωt - \cos ωt \right] (1)
\]

with the n-th order Bessel functions Jₙ(x). Thus, the difference of the analyzer settings for vanishing ω-signal for light, reflected from the reference mirror and from the sample gives the Kerr-rotation θₖ of the sample. The reference mirror was an evaporated gold film, which in a field of 10 T shows a Kerr-rotation and ellipticity of less than 0.02° in
the whole energy range [15].

The Kerr-ellipticity $\varepsilon_K$ has been measured in the same way as the rotation but with a Soleil Babinet compensator introduced between sample and modulator. Keeping the fast axis of the compensator with $\lambda/4$-retardation parallel to the major axis of the light ellipse, the light becomes linearly polarized with a rotation of $\varepsilon_K$ after passing the compensator (Senarmont principle) [16]. The difference of the analyzer settings — nulling the $\omega$-signal for sample and reference — gives the Kerr-ellipticity $\varepsilon_K$. The Kerr-rotation of the sample has to be compensated by setting the polarizer at $-\theta_K(\hbar\omega)$.

The absolute error of this method depends on the adjustment of the light path and amounts to less than a few hundredth of a degree. It originates in the difference in Faraday-rotation of the lenses, if the reference and sample light beams are slightly misaligned. The relative error of adjacent points, however, is certainly less than 1%. The sensitivity is 0.001° at all photon energies except those at both ends of the spectrum, where it increases to a few hundredth degree.

3. THEORETICAL BACKGROUND

3.1 Optical Constants and the Polar Magneto-Optical Kerr-Effect

In the geometry of the polar Kerr-effect, i.e. the vector of light propagation $\vec{q}$ as well as the applied magnetic field $\vec{H}$ are perpendicular to the sample surface, the eigenstates of light are right (+) and left (-) hand circular polarizations. In general, the coefficients of reflection $r_{\pm}=|r_{\pm}|e^{i\delta_{\pm}}$ of these modes are different, resulting in a Kerr-rotation $\theta_K=(|r_+|-|r_-|)/(|r_+|+|r_-|)$ and a Kerr-ellipticity $\varepsilon_K=(\phi_+-\phi_-)/2$.

To obtain information about the electronic structure, one needs a relation between the measured values $\theta_K$ and $\varepsilon_K$ and microscopic quantities like the electronic density of states, spin-polarization, transition probability etc. Unfortunately, there is no direct connection of these microscopic quantities to $\theta_K$ and $\varepsilon_K$, but they are related to the conductivity tensor $\sigma_{ij}$ (or the dielectric tensor $\epsilon_{ij}=\delta_{ij}-i\varepsilon\sigma_{ij}/\omega$) as will be shown in sec. 3.2.
For crystals with cubic symmetry and $\mathbf{q}$, $\mathbf{H}$ parallel to the z-axis, the conductivity tensor $\sigma$ has the following form:

$$
\sigma = \begin{pmatrix}
\sigma_{xx} & \sigma_{xy} & 0 \\
-\sigma_{xy} & \sigma_{xx} & 0 \\
0 & 0 & \sigma_{zz}
\end{pmatrix}.
$$

(2)

The absorptive parts of the complex tensor elements $\sigma_{ij}=\sigma_{ij}+i\sigma_{ij}$ are $\sigma_{1xx}$ and $\sigma_{2xy}$ as can be shown by a decomposition of $\sigma$ into the hermitian and antihermitian contribution [17]. From the Onsager relation $\sigma_{ij}(H)=\sigma_{ji}(-H)$ and the antisymmetry $\sigma_{ij}=-\sigma_{ji}$, it follows, that $\sigma_{xx}$ and $\sigma_{xy}$ are even and odd in $H$, respectively. Thus, to first order in $H$, the diagonal element $\sigma_{xx}$ is independent of the applied field and $\sigma_{xy}$ is a linear function in $H$.

For the off-diagonal conductivity, one finds in a straightforward calculation the following relation to the polar Kerr quantities $\theta_K$ and $\varepsilon_K$:

$$
\sigma_{1xy} = \frac{\omega}{4\pi} \left[ -\theta_K(3n^2k-k^3-k) - \varepsilon_K(n^3-3nk^2-n) \right]
$$

$$
\sigma_{2xy} = \frac{\omega}{4\pi} \left[ \theta_K(n^3-3nk^2-n) + \varepsilon_K(3n^2k-k^3-k) \right].
$$

(3)

In these equations, $n$ and $k$ are the refractive and absorption index, respectively. They are related to the diagonal conductivity $\sigma_{xx}$ by:

$$
\sigma_{1xx} = 2nk\omega/4\pi
$$

$$
\sigma_{2xx} = (n^2-k^2-1)\omega/4\pi.
$$

(4)

The real and imaginary part of $\sigma_{xy}$ obey the well known Kramers-Kronig formula [18]

$$
\sigma_{1xy}(\omega) = -\frac{2}{\pi} \int_{0}^{\omega} \frac{\sigma_{2xy}(\omega')d\omega'}{\omega^2-\omega'^2}
$$

$$
\sigma_{2xy}(\omega) = \frac{2\omega}{\pi} \int_{0}^{1} \frac{1}{\omega^2-\omega'^2} \sigma_{1xy}(\omega')d\omega'.
$$

(5)

This relation can be used for a rough extrapolation of $\sigma_{xy}$ below the lower energy limit of the measurement. For this purpose, an extrapolation of $\sigma_{1xy}$ below 0.5eV is chosen in such a way, that eq.(5) reproduces the measured $\sigma_{2xy}(\omega)$ in the energy range above 0.5eV, and vice versa. We
have found that, in the case of the present materials, the calculated \( \sigma_{xy} \) in the energy range from 0.5eV to 2.5eV depends quite strongly on the chosen extrapolation.

At zero frequency, \( \sigma_{2xx} = \sigma_{2xy} = 0 \) [19] and \( \sigma_{1xx} \) and \( \sigma_{1xy} \) are related to the DC-resistivity \( \rho_{xx} \) and the Hall-resistivity \( \rho_{xy} \) to first order in \( H \) by

\[
\sigma_{1xx}(0) = \frac{1}{\rho_{xx}} \quad \sigma_{1xy}(0) = -\frac{\rho_{xy}}{\rho_{xx}^2}.
\] (6)

These relations may give additional hints how to extrapolate \( \sigma_{xy} \) below the lower energy limit of the measurement.

It should be mentioned, that the coefficients of \( \theta_K \) and \( \varepsilon_K \) in eq.(3) are quite complicated functions of \( n \) and \( k \). In contrast to remarks in refs.[20] and [21] it is not possible to make any statement about a dominant contribution of either \( \theta_K \) or \( \varepsilon_K \) to \( \sigma_{1xy} \) or \( \sigma_{2xy} \). This can easily be seen from fig.3, which shows a plot of \( n^3-3nk^2-n \) and \( 3n^2k-k^3-k \)

---

**Fig. 3:** Coefficients of \( \theta_K \) and \( \varepsilon_K \) in the calculation of \( \sigma_{xy} \) (eq.(3)) as a function of \( n \) and \( k \). Solid lines: \( x=n^3-3nk^2-n \). Dashed lines: \( x=n^3-3nk^2-n \).
versus $k$ for different values of $n$. Even for $n \gg k$ or $n \ll k$, none of the functions becomes dominant. With these complications in mind it becomes clear, that a direct interpretation of $\theta_K$ and $\epsilon_K$ may lead to faulty results. This fact shall be illustrated by a comparison of two materials, both showing a strong f-d interband transition at 0.8 eV. This transition displays a diamagnetic line shape in $\sigma_{xy}$ and a similar width for both compounds which is visualized by the comparison of $\sigma_{xy}(\omega)$ for UAs and UAsSe in figs.4a and 4b. Due to different $n(\omega)$ and $k(\omega)$, the measured Kerr-rotation and -ellipticity no longer exhibit these similarities for the two materials (figs. 4c and 4d).

Fig. 4: Off-diagonal conductivity (a,b) and complex polar Kerr-effect (c,d) of UAs and UAsSe single crystals at $B=10T$, $T=20K$ and $B=5T$, $T=10K$, respectively. An analysis of these data is given in secs. 4.2.2 and 6.
3.2 Microscopic Theory

After the enormous progress in theoretical work about the magneto-optical response of magnetically ordered materials in the 60's and early 70's, there has been a stagnation in the development of theoretical concepts in the last ten years. Therefore, only the basic ideas of theoretical models which are necessary to interpret the magneto-optical response of uranium compounds are presented in the following and appropriate references will be given.

It has been shown by several authors [22-27] that the large magneto-optical effects observed for ferromagnets can not be explained simply considering the Zeeman perturbation on the initial and final states as it is generally done for nonmagnetic materials [28] but needs the introduction of spin-orbit coupling. The influence of spin-orbit coupling has been considered as a perturbation of either the initial [23] or the final [22] state energies of an interband transition or as a modification of the initial state wavefunctions [29] which is of importance if the ground-state orbital momentum is quenched.

It has been pointed out that in general the magneto-optical effects will be proportional to

$$\sum \bar{s}_i \times \mathbf{V} \bar{p}_i$$

(7)

which is the spin-orbit energy of an electron with spin $\bar{s}$ and momentum $\bar{p}$ moving through the electrical field $-\mathbf{V}$. This vector sum clearly evidences, that the magneto-optical effects are proportional to the product of magnetization $\sum \bar{s}_i$ and spin-orbit energy, i.e. apart from a sufficient spin-orbit splitting, a high spin polarization is required to obtain a large magneto-optical response.

Based on these ideas, Erskine and Stern [27] have developed expressions for $\sigma_{xy}$ which allow quantitative calculations for interband and intraband transitions.

3.2.1 Conduction Electrons

It has been shown [27,30], that intraband transitions may contribute to $\sigma_{xy}$ with two different frequency dependences, $\sigma_{2xy} \omega^{-1}$ and $\omega^{-3}$. The theory gives a proportionality of $\sigma_{xy}$ to the conduction electron con-
centration via the plasma frequency $\omega_p^2=4\pi n_e^2/m^*$ and to their spin polarization $\sigma_d=(n^+-n^-)/(n^++n^-)$. $n^+$ and $n^-$ are the number of conduction electrons with spin moment parallel and antiparallel to the total moment, respectively. In addition, the second term of $\sigma_{xy}$ is proportional to the strength of the spin-orbit coupling via $P_0/eV_0$ [27]:

$$\sigma_{xy}(\omega) = \frac{\omega_p^2}{4\pi} \sigma_d \left[ \frac{-Q}{\Omega^2+(1/\tau+i\omega)^2} \right] \frac{P_0}{eV_0} \left[ 1 - \frac{i\omega(1/\tau+i\omega)}{\Omega^2+(1/\tau+i\omega)^2} \right].$$

In this equation, $\tau=1/\tau$ and $Q$ are the relaxation and the skew-scattering frequency, respectively. Consequently, the absorptive part of the free electron contribution is given by

$$\sigma_{2xy}(\omega) = \frac{\omega_p^2}{4\pi} \sigma_d \left[ \frac{2\gamma Q\omega}{(\Omega^2+\gamma^2-i\omega^2)^2+4\gamma^2\omega^2} \right] \frac{P_0}{eV_0} \left[ \frac{\omega Y(\Omega^2+\gamma^2+i\omega^2)}{(\Omega^2+\gamma^2-i\omega^2)^2+4\gamma^2\omega^2} \right].$$

It is interesting to note, that the first term on the right side corresponds to the classical Drude theory if $\sigma_d Q$ is replaced by the cyclotron frequency $\omega_c$. This first term manifests itself by different plasma frequencies for right and left circularly polarized light. The skew-scattering frequency $Q$ has been shown to coincide with the spin-orbit parameter $\zeta_{SO}$ [30].

The decisive number for the dominance of the first or the second term in eq.(9) at a frequency $\omega$ is the ratio $(|P_0|/eV_0)/(\Omega/\omega^2)$. This ratio can be estimated using the relation

$$P_0/eV_0 = (ma^2\omega_{SO})/(\hbar\omega_{ab}).$$

Here, $a$ is the lattice constant and $\hbar\omega_{SO}$ and $\hbar\omega_{ab}$ are typical spin-orbit and interband energies, respectively [31].

In conclusion, the analysis of the free electron part enables the determination of the sign of the conduction electron spin-polarization $\sigma_d$ from the sign of $\sigma_{xy}$ and it gives information on the size of $\sigma_d$, the number of conduction electrons $N$ and the magnitude of the relaxation frequency $\gamma$.

3.2.2 Interband Transitions

The modified atomic model of Erskine and Stern [27] for an interband
transition $a \leftrightarrow b$ introduces the total weight

$$\langle \sigma_{xy} \rangle = \int |\sigma_{xy}|^2 d\omega_{a+b}$$

of this transition, which is given in atomic theory by:

$$\langle \sigma_{xy} \rangle = \pi N e^2 \sum_{\alpha \beta} \left( \omega_{x\beta}^+ |\langle \beta | x-i\gamma | \alpha \rangle |^2 - \omega_{x\beta}^- |\langle \beta | x+i\gamma | \alpha \rangle |^2 \right) \sigma_j\sigma_{m\alpha \beta}. \quad (12)$$

In this equation, $\alpha$ and $\beta$ are the spin-orbit split sublevels of $a$ and $b$, respectively, and $\sigma_j$ is the joint spin polarization of the initial and final state.

The dipole matrix elements are nonzero only for transitions with $\Delta m = \pm 1$.

Assuming a fixed spin moment $m_3$ due to strong exchange forces, the spin-orbit coupling lifts the degeneracy of the orbital quantum number $m_1$:

$$E_{m=0}^m = \zeta_{m0} m_1.$$ 

(13)

The calculation of the dipole matrix elements for right and left hand circularly polarized light in eq.(12) is performed within the approximation, that the atomic oscillator strength of the transition $a \leftrightarrow b$ is unchanged in the solid, but smeared out over the band-width $E_B$. In this approximation the initial and final state wavefunctions are spherical harmonics $Y_{jm}$ for the orbital part, multiplied by a radial contribution $u(r)$ and it follows:

$$\Sigma_{\alpha \beta} |\langle \beta | x-i\gamma | \alpha \rangle |^2 - |\langle \beta | x+i\gamma | \alpha \rangle |^2 = \Sigma_m \left( |\langle Y_{m+1}^{m-1} | x-i\gamma | Y_{m}^{m} |^2 - |\langle Y_{m+1}^{m+1} | x+i\gamma | Y_{m}^{m} |^2 \right) R_{ab}^2. \quad (14)$$

Here, $R_{ab}^2$ is the radial overlap integral

$$R_{ab}^2 = \left| \int u_a u_b r^2 dr \right|^2. \quad (15)$$

The comparison of the off-diagonal weight $\langle \sigma_{xy} \rangle$ with the total diagonal weight $\langle \sigma_{xx} \rangle$ of the interband transition $a \leftrightarrow b$, which is given by
shows up, why the combination of optics and magneto-optics is a powerful method for the investigation of the electronic structure of magnetic solids: while all electronic states contribute to eq.(16), only those states showing a net spin-polarization contribute to eq.(12). However, also unpolarized but exchange split states may contribute to the magneto-optical response but with a much smaller signal [8, 27].

It is noteworthy to mention, that the maximum value of \( \langle \sigma_{xy} \rangle / \langle \sigma_{xx} \rangle \) is 2/3. This fact can easily be seen, writing \(|\vec{r}|^2 = |(x+iy)/2|^2 + |(x-iy)/2|^2 + |z|^2\) in eq.(16). In the presented modified atomic model, maximum \( \langle \sigma_{xy} \rangle \) is reached for \( \sigma_j=1 \) and \( E_{so}/E_B=1 \) [27].

Finally, the diagonal and off-diagonal oscillator strengths \( f_{xx} \) and \( f_{xy} \), respectively, are defined by

\[
\begin{align*}
   f_{xx} &= \frac{\langle \sigma_{xx} \rangle}{N} \\
   f_{xy} &= \frac{\langle \sigma_{xy} \rangle}{N}
\end{align*}
\]

This characteristic quantity of an interband transition is independent of the density of molecules \( N \) in the crystal and therefore it is more suitable than the total weight for a comparison of the same transition in different materials.

4. BINARY AND PSEUDO-BINARY COMPOUNDS \( UX_xZ_{1-x} \)

\( (X = S, Se, Te; Z = P, As, Sb; 0 < x < 1) \)

4.1 Introduction

The face centered cubic uranium-monochalcogenides and -monopnictides are certainly the most investigated class of actinide compounds. This fact reflects on one hand the relative easy handling of these materials from both the experimental and theoretical point of view, and on the other hand the large variety of physical effects encountered in these systems. In some way, this class of materials can be thought of as a model system...
for the understanding of uranium compounds at all.

The uranium chalcogenides as well as a great variety of mixed crystals $U\chi Z_{1-x}$ are ferromagnets [32]. The magnetic moments are strictly confined to the (111)-easy axis and the total moment increases going from $US$ to $U\text{Te}$. The moment obtained from magnetization measurements is found to be smaller than the neutron moment, which has been interpreted by antiparallel d and f contributions [33].

The uranium pnictides and some other mixed crystals, on the other hand, order antiferromagnetically [32]. In general, they exhibit a very complex magnetization-field-temperature phase diagram, showing various multiple-k antiferro- and ferrimagnetic phases. Especially the phase diagram of $U\text{As}$ has been intensively studied by neutron scattering [34]. The magnetic parameters of the UX and UZ compounds are summarized in fig.5.

![Fig. 5: Ordering temperature $T_{C, N}$, paramagnetic moment $\mu_{\text{eff}}$, magnetization moment $\mu_{\text{tot}}$ and neutron moment $\mu_{n}$ of uranium-chalcogenides and pnictides [32, 34-42].](image)

The complex magnetic behavior of $U\chi Z_{1-x}$ goes along with an unusual electronic structure. One characteristic feature is the spatially extended nature of the uranium f wavefunctions and their proximity to the Fermi level [43]. The metallic conductivity, however, is predominantly due to occupied d states. A cluster calculation for $US$ has indicated the formation of a dip in the d density of states near $E_{F}$ [44] due to a strong
fd hybridization. Recently, this theoretical prediction has been confirmed by a spin-polarized APW band structure calculation for UN [45]. In addition a large fp hybridization is expected for the pnictides (x=1), decreasing with decreasing x because of a shift of the p band center to higher binding energies with decreasing covalency [46,47].

While for the compounds with small anions, i.e. US and UP, this view of the electronic structure seems to be well established, there are large discrepancies in the interpretations of different experimental results for compounds with heavier anions [43]. Optical [46], specific heat [48] and some photoemission [49-53] results favour band like f states with a decreasing width going from US to UTe and UP to USB, respectively, while other photoemission data on USE, UTe, UAs and USB [54] have been interpreted in a 'quasi'-localized picture. The paramagnetic moment of all materials, derived from the Curie-Weiss law at T >> TC, can not be interpreted by Hund's rule localized f2 or f3 states, but increases continuously with heavier anions (fig.5).

Regarding the electronic structure of these compounds, the aim of the present work is i) to provide a systematic magneto-optical study of the electronic density of states in the vicinity of Ef; ii) to shed light on a possible localization of the f states with increasing spatial separation of the uranium atoms; iii) to obtain results on the magnetic exchange and spin-polarization of d and f electrons and iv) to get information about the strength of hybridization effects between f states and p,d electrons.

In sec. 4.2, the optical and magneto-optical behavior of UAsxSe1-x is discussed to point out similarities and differences in the electronic structure of uranium chalcogenides and pnictides. In sec. 4.3, the magneto-optical data along the chalcogenides and pnictides series are presented and trends of the electronic structure along these series will be examined. Magnetic exchange in uranium pnictides, but especially in the system USBxTe1-x is studied in detail in sec. 4.4. Finally, magneto-optics as a powerful technique for the study of magnetic phase transitions is demonstrated in sec. 4.5 for UAs.

4.2 Similarities and Differences in the Electronic Structure of Uranium-Chalcogenides and Pnictides: UAsxSe1-x

UAs and USE form a continuous series of solid solutions crystallizing in the rocksalt structure with a nearly constant lattice parameter a=5.75A
UAs is an antiferromagnet with an Néel temperature of 124±2 K. At about \( T_N/2 \), it undergoes a first order phase transition from a ++-- (type I) to a ++++ (type IA) stacking of ferromagnetic (001)-planes. At this phase transition, a 10\% decrease of the magnetic moment of the uranium ion has been observed [56]. Recent neutron experiments have shown, that the IA to I transition is accompanied by a transition from a \( 2\vec{k} \) (easy axis (110)) to a \( 1\vec{k} \) (easy axis (100)) collinear spin structure, explaining the change in the magnetic moment [34]. The application of magnetic fields induces intermediate spin structures like multiple-\( \vec{k} \) ferromagnetic phases [57]. The magneto-optical determination of the magnetization-field-temperature phase diagram of UAs will be presented in sec. 4.5.

USe orders ferromagnetically below \( T_C=160 \) K [58]. The easy direction is the (111)-axis. No rotation of the magnetization out of this direction could be observed by the application of fields up to 15 T. This evidences the existence of very strong anisotropy fields.

4.2.1 Optical Properties

The optical conductivity of UAs\(_{0.7}\)Se\(_{0.3}\) (fig. 6) shows features,
which are typical for UX and UZ compounds [46]. The free electron contribution is weak relative to the expected number of conduction electrons and is highly damped. The plasma energy lies between the values observed for UAs and USe [46]. Two strong interband transitions (peaks A and B) dominate the low energy conductivity while the broad and structured absorption band around 7.5 eV is attributed to valence-band excitations [46].

To compare with the magneto-optical data, we will focus on the low energy range (0.5 - 6 eV). A quantitative analysis including the decomposition of the diagonal conductivity into a free electron part and different Lorentzian shaped interband transitions [59] gives the following results:

i) Peak A has in all three compounds the same transition energy $\hbar\omega_A=1.0\pm0.02$ eV, the same width $\hbar\gamma=1.15\pm0.05$ eV and the same oscillator strength $f=0.9\pm0.02$. This points to identical initial and final states for this excitation in the different compounds. ii) Peak B decreases in oscillator strength by about a factor of three going from USe to UAs, while its energy $\hbar\omega_B=2.4\pm0.2$ eV and its width $\hbar\gamma=2\pm0.3$ eV remain constant. iii) Substituting As by Se, peak C1 at about 4 eV in UAs weakens at constant energy and at about 5.5 eV a new peak C2 develops.

4.2.2 Magneto-Optical Properties

4.2.2.1 Experimental Results

In sec. 3.2 it has been argued, that the polar Kerr-effect is proportional to the magnetization of the sample volume, which is probed by this technique. The penetration depth of the light beam is roughly given by the absorption constant $K$ [cm$^{-1}$]:

$$d = \frac{1}{K} = \frac{\lambda}{4\pi k}$$

(18)

and amounts to 200-1000Å in metals. Thus it can be expected, that in general the size of the polar Kerr-effect is a measure of the bulk magnetization and, on the other hand, deviations from the bulk behavior indicate sample imperfections for the first few hundredth of Å.

Fig. 7 shows the temperature dependence of the Kerr-rotation of UAs, UAs$_{0.7}$Se$_{0.3}$ and USe which enlightens the complex magnetic phase diagram in the system UAs$_x$Se$_{1-x}$.

The simplest case is USe for which the temperature dependence of $\theta_k$ shows a typical ferromagnetic behavior (fig. 7a) with $M(111)=1.81\mu_B/U$.
at 15 K and 4 T \([58]\). UAs orders antiferromagnetically and thus only very small magneto-optical effects are found in lower fields. However, UAs undergoes a magnetic phase transition at 8.7 T (see also sec. 4.5). In the high-field induced ferrimagnetic phase, the magnetic moment reaches \(M(100)=0.42 \mu_B/\text{U}\) at 10 T and 20 K. Consequently, the observed Kerr-rotation is about a factor of three smaller than in USe (fig. 7c). With increasing temperature different ferri- and antiferromagnetic phases can be observed which will be discussed in detail in sec. 4.5.

In a field of 5 T, the mixed compound UAs\(_{0.75}\)Se\(_{0.3}\) shows four magnetic phases as a function of temperature (fig. 7b): paramagnetic behavior for \(T>T_N=127 K\), a ferromagnetic phase between \(T_N\) and about 115 K and two different antiferromagnetic regions at lower temperatures \([55]\). The highest magnetization occurs in the ferromagnetic phase at 123 K and amounts to \(M(100)=0.48 \mu_B/\text{U}\).

To obtain the highest resolution the magneto-optical spectra to be repor-
tions have been measured at that temperature, which gives the largest signal. Fig. 8 displays the energy dependent complex polar Kerr-effect for the three compounds. The spectra all look very similar, each with two structures in $\theta_K$ and $\varepsilon_K$. Yet, because $\theta_K$ and $\varepsilon_K$ are linear combinations of absorptive and dispersive quantities, the interpretation in terms of the electronic structure is not straightforward. Instead, the real and imaginary part of the off-diagonal conductivity $\sigma_{xy}$ shown in fig. 9 should be discussed. In this figure, an extrapolation of $\sigma_{xy}$ for energies less than 0.5 eV is included taking advantage of the Kramers-Kronig relation between $\sigma_{1xy}(\omega)$ and $\sigma_{2xy}(\omega)$ (sec. 3.1, eq. (5)).

Up to about 2.5 eV the off-diagonal conductivity of the three materials displays large similarities. At higher energies, no magneto-optically active excitations are observed in USe, but there appears a broad peak C1 around 3 eV with increasing As concentration.

Fig. 8: Energy dependent polar Kerr-rotation $\theta_K$ and -ellipticity $\varepsilon_K$ for (100)-oriented cleaved single crystals of UAs, UAs$_{0.75}$Se$_{0.3}$ and USe. Note the change of the ordinate scale for USe.
4.2.2.2 Conduction Electrons

A comparison of the energy of peak A in $\sigma_{xx}$ and $\sigma_{xy}$ (sec. 4.2.2.3) indicates, that the line shape of this lowest energy interband transition A has to be 'diamagnetic', i.e. it shows a bell shaped form with a maximum in $\sigma_{xy}$ at $\hbar \omega_A$ and $\sigma_{2xy}(\hbar \omega_A)=0$. Consequently, the free electron contribution to $\sigma_{2xy}$ must be positive, which is equivalent to a negative spin-polarization of the conduction electrons (eq. 9), i.e. the number of d electrons with spin moment antiparallel to the f moment is larger than the number of those with parallel spin moment. This holds for ferromagnetic USe and UAs$_{0.7}$Se$_{0.3}$ as well as for ferrimagnetic UAs and it constitutes the first experimental determination of the conduction electron spin-polarization for an uranium pnictide. It agrees with the result of a spin-polarized band structure calculation for UP [60]. In the case of USe, the negative polarization is in qualitative agreement with a
calculation for US [44] and with spin-polarized photoemission results [61].

To derive the size of the spin-polarization from the free-electron contribution, several parameters occurring in eq. (9) have to be estimated. First, comparing the two terms on the right side of this equation, we note that at \( \hbar \omega = 1 \text{ eV} \) their ratio \([30](P_0/e_v)/(Q/\omega^2)\) amounts to \( \approx 10 \) for our compounds. Thus we neglect the first term in the following.

Using eq. (10) the spin-orbit contribution \( P_0/e_v \) in eq. (9) may be calculated. Taking \( a = 1.5 \text{Å} \) for the atomic radius [44] and \( 1 \text{ eV} \) for both the spin-orbit energy \( \hbar \omega_{SO} \) and the lowest interband energy \( \hbar \omega_{AB} \), one obtains \( P_0/e_v \approx 2 \times 10^{-16} \text{ sec} \). Taking for the conduction electron relaxation frequency at low temperatures \( \eta = 0.5 \text{ eV} \), the product of spin-polarization and conduction electron concentration is found to be \(-41\), \(-13\) and \(-12\) \( \% \) electrons/formula unit for US, UAs\(_0.7\)Se\(_0.3\), and UAs, respectively. The solid and dash-dotted curve in fig. 9 display the corresponding free electron contributions to \( \sigma_{xy} \). To obtain the size of the spin polarization alone, one needs to know the conduction electron concentration. Assuming for US 1.1 electrons per formula unit (this number will be discussed in sec. 4.3.2.1), and scaling the conduction electron concentration with either the square of the plasma energy or with the intensity of the \( d+f \) transition (see sec. 4.2.2.3) within the \( \text{UAs}_x\text{Se}_{1-x} \) series, spin-polarization values of \(-35\)\%, \(-20\)\% and \(-30\)\% are derived for the three compounds with increasing \( x \) and the magnetic fields given in fig. 7.

These numbers express very interesting physical properties of the \( d \)-conduction band and the \( f-d \) exchange. The observed macroscopic \( d \)-spin-polarization for UAs, for example, has to be viewed in the context of the low macroscopic magnetization in the ferrimagnetic phase, amounting to 0.42 \( \mu_B / \text{U} \). This means, that the local \( d \)-spin-polarization, in the vicinity of the \( f \) moment, must be \( \approx -100\% \). This idea is visualized in fig. 10, which shows a simple ferrimagnetic \( f \)-spin structure and \( d \)-electrons, which are \(-100\% \) spin polarized locally. The macroscopic conduction electron spin-polarization, however, is given by summing over all \( d \) electrons, i.e. amounts to \(-33\% \).

Assuming the same hypothetical saturation magnetization for UAs, UAs\(_0.7\)Se\(_0.3\), and US\(_e\) of 1.8 \( \mu_B / \text{U} \), one finds a local spin polarization of \(-100\)\%, \(-75\)\% and \(-35\)\%, respectively. Because of some ambiguity in the determination of \( n \), \( n_0 \) and of the total moment, these values should be viewed as showing up a tendency and not as exact numbers.

In a first approach, the conduction band in a magnetized solid is split
Fig. 10: Model for the explanation of the high conduction electron spin-polarization in uranium-monopnictides. The macroscopic d spin-polarization for the displayed ferrimagnetic structure (UAs) amounts to -33%, if a -100% local spin polarization is assumed.

into two subbands with opposite spin direction. Assuming a rectangular density of states of 1 electron/eV-spin, the two subbands have to be energetically split by at least 0.4 eV to obtain -100% spin polarization and an occupation of ~0.4 electrons/U (fig. 11) as it has been observed for UAs.

Fig. 11: Simple sketch of the spin-polarized conduction electron density of states which allows the interpretation of magneto-optical data. The assumed Fermi energy for UAs, UAs$_{0.7}$Se$_{0.3}$ and USe is visualized by the dashed horizontal lines.

It is interesting to note, that the simple idea of the filling of a rigid band can account for both the decrease in spin polarization and the in-
creasing occupancy in going from UAs to USe. The dashed horizontal lines in fig. 11 indicate $E_F$ for UAs$_{0.7}$Se$_{0.3}$ and USe for the measured d electron numbers of 0.65 and 1.1 electrons/U, respectively. The obtained spin polarization in this model amounts to -65% and -35%, which compares favourably with the magneto-optical results.

The observed negative conduction electron spin polarization and the two subband model leads to an important prediction for the f+d transition energy. If the f-moment is mainly spin-like it follows, that the f+d transition energy should increase by 0.2 eV comparing unmagnetized UAs with magnetized UAs, i.e. a blue shift is predicted (fig. 12). However, as we will show in secs. 4.2.2.3 and 4.4, we observe a red-shift of this magnitude. Thus if follows, that the f moment is not determined by the spin, but the orbital moment, i.e. it obeys Hund's rules of antiparallel $L$ and $S$ for less than seven f electrons (see also sec. 4.4). This is a first direct experimental corroboration of a recent theoretical work on UN, proposing a dominant orbital moment contribution to 5f band magnetism [7].

Fig. 12: Model of the atomic f and d states for an unmagnetized (a) and a magnetized (b,c) solid. A dominant f spin moment results in a blue-shift of the f+d transition energy (b) whereas a dominant orbital f moment predicts a red-shift (c).
4.2.2.3 Interband Transitions

The pure interband contribution to $\sigma_{xy}(\omega)$ is the difference of the measured $\sigma_{xy}(\omega)$ and the free electron contribution. It is dominated by a 'diamagnetic' transition A with exactly the same line width (FWHM=0.7 eV) but different transition energies for USe, UAs$_{0.7}$Se$_{0.3}$ and UAs (tab. 1). The total weight (eq. 11) is about a factor of four less for UAs than for USe which corresponds approximately to the ratio of the total magnetic moments and not to the ratio of the moments along the (100)-direction as it would be expected [62].

<table>
<thead>
<tr>
<th></th>
<th>UAs</th>
<th>UAs$<em>{0.7}$Se$</em>{0.3}$</th>
<th>USe</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\hbar\omega_A$ [eV]</td>
<td>0.82</td>
<td>0.86</td>
<td>0.94</td>
</tr>
<tr>
<td>$&lt;\sigma_{2xy}&gt;$ $[10^{-23} \text{sec}^{-2}]$</td>
<td>2.3</td>
<td>2.3</td>
<td>9.0</td>
</tr>
<tr>
<td>$\mu_{tot}$ [$\mu_B$]</td>
<td>0.42</td>
<td>0.48</td>
<td>1.8</td>
</tr>
</tbody>
</table>

Table 1: Observed transition energy $\hbar\omega_A$ in $\sigma_{xy}$ and integrated weight $<\sigma_{2xy}>$ of transition A in the magnetically ordered phases (magnetization $\mu_{tot}$) of the three compounds. The field and temperature conditions are given in fig. 9.

In $\sigma_{xx}$ as well as in $\sigma_{xy}$, we assign peak A to a transition from a narrow f band at $E_F$ into d states. This interpretation is substantiated by the following arguments:

i) Peak A is present in the optical spectrum ($\sigma_{xx}$) of UAs as well as of USe with the same line-shape and the same oscillator strength; ii) in $\sigma_{xy}$, this transition again has the same line shape and the size of the peak is proportional to the magnetic moments in the different compounds; iii) the large size of the magneto-optical response points to an excita-
tion of 'magnetic' electrons with large spin-polarization; iv) eqs. (12) and (16) describe the experimental oscillator strengths and line-shapes for $\sigma_{1xx}$ and $\sigma_{2xy}$ which will be discussed in sec. 4.3.2.2. These equations result in an $f$ occupancy, $n_f$, which is by about a factor of 2 less than the expected occupancy assuming $n_f=4-n_d$ in USe and $n_f=3-n_d$ in UAs. This is a clear indication of non-negligible correlation effects [63] in the narrow $f$ band; v) the absence of any fine structure in oxy which would be expected for strictly localized $f$ states [8,10], on the other hand, points to an $f$ band width in excess of typical spin-orbit energies.

We have already mentioned in the last section, that one further interesting feature of the $f$+$d$ transition in UAs$_x$Se$_{1-x}$ is the different resonance energy $\hbar\omega_A$ in $\sigma_{xx}$, observed at $T=300K$ for $B=0T$ and in $\sigma_{xy}$, observed for $T<T_F$ and $B=0$. Such large magnetization induced redshifts were up to now only observed in some ferro- and antiferromagnetic semiconductors [9]. The maximum shift is 0.3 eV in EuO. Yet, it was found for EuO doped with Gd, that the red-shift decreases with increasing conduction electron concentration [64]. Applying a similar argument to our UAs$_x$Se$_{1-x}$ system, UAs should exhibit the largest red-shift which is actually the case. Unfortunately, the evolution of the entire 0.17 eV shift in UAs as function of magnetization is hard to follow up in detail because of the complex magnetic phase diagram of UAs and the rather small magneto-optical signals in the antiferromagnetic phases. This problem is less difficult in UAs$_x$Se$_{1-x}$ for $x<0.7$ and we have measured the Kerr-rotation maximum which corresponds to peak A in $\sigma_{xy}$ as a function of magnetization. Fig. 13 displays the photon energy dependence of the Kerr-rotation at $T=123K=T_N$ normalized to its maximum value for different magnetic fields. We observe, that the red-shift of the $f$+$d$ transition saturates at a field of $\approx 5 T$ and amounts to about 0.14 eV. To our knowledge, the As-rich UAs$_x$Se$_{1-x}$ compounds are the first metals showing such a striking magneto-optical effect. The same effect, but even more pronounced, is presented for USb$_x$Te$_{1-x}$ in sec. 4.4.

Moving our attention to higher photon energies, we find at $\approx 2.3$ eV peak B with a 'paramagnetic' line shape in all materials. The total weight of this peak decreases from USe to UAs by a factor of about 6. The initial and/or final states of this transition have to possess a net spin-polarization, which is responsible for the observed large magneto-optical re-
Fig. 13:
Normalized Kerr-rotation of UAs$_{0.7}$Se$_{0.3}$ at $T=123$ K for different applied fields in the energy range of maximum rotation (transition A).

response. In addition, the oscillator strengths, normalized with the respective magnetizations, decrease nearly proportionally to $\omega_p^2$, i.e. they are proportional to the number of d electrons. Both facts point to an interpretation in terms of a d+f transition. The occurrence of a strong d+f transition, however, can only be expected, if the f states are not localized [63]. Consequently, the observation of this transition with equivalent strength in UAs$_x$Se$_{1-x}$ corroborates similar f delocalization for different x. On the other hand as it will be shown in sec. 4.3.2.3, the same excitation shows a drastic decrease in oscillator strength along the uranium-chalcogenide and pnictide series, indicating the increase of f localization for UX and UZ compounds with heavier anions.

Peak C1 around 3 eV in fig. 9 has also a 'paramagnetic' line shape but it is only present in the As-rich samples. The width of this transition increases with the As concentration. Its energy agrees roughly with the energy of peak C1 in the diagonal conductivity (fig. 6). Peak C2, however, which is clearly resolved in $\sigma_{1xx}$ for USe around 5 eV, has no corresponding signal in $\sigma_{xy}$. At first sight the strong magneto-optical response of this transition for UAs and its absence for USe is an unexpected result. To understand this behavior, let us examine somewhat closer the p valence-band in the system under discussion.

Band structure calculations [44,47,65] find the valence-band of UAs and USe centered at binding energies of about 3 eV and 5 eV, respectively. In addition, due to a strong admixture of some f and merely d states to the
p states, a nonuniform distribution of angular momentum throughout the band is predicted for the pnictides with more high-\( l \) states at the top and more low-\( l \) states at the bottom [47]. This admixture is smaller for the chalcogenides because of the higher p binding energy and the smaller charge transfer necessary to fill the valence band. Thus, the peaks C1 and C2 in \( \sigma_{x^2} \) (fig. 6) are interpreted as the onset of excitations from the top of the valence band. These transitions are magneto-optically active for strong f,d admixtures and we assign peak C1 in \( \sigma_{xy} \) (fig. 9) to a (pd)+f transition.

Comparing our results with different photoemission studies on UAs and USe, we find in general good agreement [49,50,61]. In particular, the energy separation of high-\( l \) and low-\( l \) valence states for the uranium-pnictides has also been deduced from energy dependent UPS measurements [50]. On the other hand, in a more recent UPS study on UAs\(_x\)Se\(_{1-x}\) [54] two emission peaks, one close to \( E_F \) and one 0.7 eV below \( E_F \) have been interpreted as a final state splitting of localized 5f states and large differences in the \( f \) density of states between the chalcogenide and the pnictide have been claimed to exist. However, an examination of the experimental UPS results merely shows an increase of the peak intensity at 0.7 eV binding energy going from UAs to USe which in the light of our magneto-optical measurements reflects only an increase of the occupancy of the 6d conduction band [44].

4.2.3 Summary

In this section we have tried to point out similarities and differences in the optical and magneto-optical spectra of uranium-chalcogenides and pnictides by a systematic study of the evolution of the magneto-optical properties as a function of the As content in the pseudo-binary compound UAs\(_x\)Se\(_{1-x}\). The characteristic features have been correlated to microscopic properties. The main results are:

i) an unambiguous identification of the interband transitions to be \( f+d \), \( d+f \) and (pd)+f like;

ii) the first observation of a magnetic red-shift of the \( f+d \) transition energy in a metal;

iii) an negative conduction electron spin-polarization \( \sigma_d \) both in the chalcogenide and in the pnictide. The size of \( \sigma_d \) increases with decreasing number of electrons, which can satisfactorily be explained by a rigid band filling of an exchange split d conduction band; the \( f \) state,
however, is pinned at \( E_F \).

iv) the \( f \)-magnetic moment is evidenced to be dominantly of orbital character.

4.3 Uranium Monochalcogenides and Pnictides

In the last section we have demonstrated, that the electronic structure of the uranium-chalcogenides and pnictides appears very similar in the system \( \text{UAs}_x\text{Se}_{1-x} \) from the optical and magneto-optical point of view. In this section we will show, that this observation holds in general for all \( \text{UX} \) compounds (\( \text{X}=\text{S, Se, Te, P, As, Sb} \)), but some special characteristics occur for \( \text{UTe} \) and \( \text{USb} \).

4.3.1 Optical Properties

Because the indices of refraction \( n \) and absorption \( k \) are necessary for the calculation of \( \sigma_{xy} \) from the Kerr-effect, we review briefly the optical measurements of Schoenes [46] on \( \text{US}, \text{USE}, \text{USe}, \text{UAs} \) and \( \text{USB} \) and present new data for \( \text{UP} \).

The available single crystals of \( \text{UP} \) do not show a mirror-like surface upon cleaving. Therefore the measurement of the reflected intensity at normal incidence gives poor results at higher photon energies (\( h\omega > 3.5 \) eV), which makes a Kramers-Kronig analysis inopportune. Instead, we have measured for two different angles of incidence the ratio \( R / R_1 \) of the reflectivity for light linearly polarized in or normal to the plane of incidence. (The method is described in [66, 67]). By means of Fresnel's equations we computed the refractive index \( n \) and the absorption index \( k \) from these data. A control measurement on \( \text{UAs} \) has shown good agreement in the 0.5-5 eV energy range with the optical constants obtained by Kramers-Kronig inversion of the absolute reflectivity.

Fig. 14 shows the absorptive diagonal conductivity \( \sigma_{1xx} \) for all six materials at room temperature. In this figure we have included a decomposition of \( \sigma_{1xx} \) into a free electron part and different Lorentzian shaped interband transitions:

\[
\sigma_{1xx}(\omega) = \frac{Nn \gamma}{m} \sum f \left| \begin{array}{c} \text{free} \\ \text{line} \end{array} \right| \left( \frac{\omega_i^2 - \omega^2}{\omega_i^2 - \omega^2/y_i} \right) + \frac{N \gamma}{m} \sum f \left| \begin{array}{c} \text{lorentz} \end{array} \right| \left( \frac{\omega_i^2 - \omega^2}{\omega_i^2 - \omega^2/y_i} \right)
\]  

(19)
Fig. 14: Lorentz fit of the absorptive diagonal conductivity of the uranium-monochalcogenides and -monopnictides in the energy range of the f+d and d+f transitions (solid lines) at room temperature. The fit parameters are collected in tab. 2.
In eq. (19), \( N \) is the number of molecules per cm\(^3\) and \( n \) stands for the number of conduction electrons per formula unit. The interband fit parameters are oscillator-strength \( f_i \), transition energy \( \hbar \omega_i \) and line width \( \hbar \gamma_i \). As it can easily be seen from fig. 14, an unambiguous determination of these parameters is only possible at those energies, where different transitions are clearly separated, i.e. in the energy range of the \( f+d \) and \( d+f \) transitions. Their fit values are given in tab. 2.

<table>
<thead>
<tr>
<th></th>
<th>US</th>
<th>USe</th>
<th>UTe</th>
<th>UP</th>
<th>UAs</th>
<th>USB</th>
</tr>
</thead>
<tbody>
<tr>
<td>( f+d )</td>
<td>( \hbar \omega_A ) (±0.02) [eV]</td>
<td>1.15</td>
<td>1.0</td>
<td>0.6</td>
<td>1.05</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>( \hbar \gamma_A ) (±0.05) [eV]</td>
<td>1.1</td>
<td>1.2</td>
<td>1.15</td>
<td>1.1</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td>( f_A ) (±0.02)</td>
<td>0.85</td>
<td>0.9</td>
<td>0.9</td>
<td>0.9</td>
<td>0.9</td>
</tr>
<tr>
<td>( d+f )</td>
<td>( \hbar \omega_B ) (±0.2) [eV]</td>
<td>2.75</td>
<td>2.45</td>
<td>1.75</td>
<td>2.8</td>
<td>2.3</td>
</tr>
<tr>
<td></td>
<td>( \hbar \gamma_B ) (±0.3) [eV]</td>
<td>2.8</td>
<td>2.5</td>
<td>2.1</td>
<td>2.3</td>
<td>1.9</td>
</tr>
<tr>
<td></td>
<td>( f_B ) (±0.2)</td>
<td>1.55</td>
<td>0.7</td>
<td>0.25</td>
<td>0.5</td>
<td>0.4</td>
</tr>
</tbody>
</table>

Tab. 2: Interband transition parameters used for the fit of \( \sigma_{1xx} \) in fig. 14. The values are rounded to 0.05.

Thus, from the fit of the optical data we obtain the in a sense astonishing result, that the oscillator-strength as well as the line width of the \( f+d \) transition are equal for all the six materials whereas the transition energy decreases as expected. In particular the second result is certainly unusual, because one expects a contraction of band width and band separations [68] if for a series of materials MX, the cation M is fixed and the anion is moved down along a column of the periodic system. However, the reason of this contradiction, which occurs only for the \( f+d \) transition, may be the strong f-d hybridization, which tends to keep a certain band width, i.e. the band width is determined by hybridization effects and not by the overlap of wavefunctions. This hypothesis is corroborated by a recent calculation of the f-d radial overlap integral (eq. (15)) with LMTO-wavefunctions [69] which gives \( |R_{df}|^2 = 6.6 \times 10^{-17} \text{ cm}^2 \) for US and \( 5.3 \times 10^{-17} \text{ cm}^2 \) for UTe. These numbers are about a factor of
three larger than the overlap in atomic uranium \( (2.25 \times 10^{-17} \text{ cm}^2 \ [70]) \) or for the f and d wavefunctions in UO \( (3.1 \times 10^{-17} \text{ cm}^2 \ [71]) \).

4.3.2 Magneto-optical Results

We have shown in sec. 3.2, that the Kerr-effect is proportional to the sample magnetization. Thus, to obtain a reasonable signal to noise ratio for the energy dependent measurement of \( \theta_K \) and \( \varepsilon_K \), one has to choose appropriate temperature and applied field conditions. US, USe and UTe are ferromagnets and hence exhibit a large magnetization at \( T \ll T_C \). The applied field is necessary to obtain a one-domain sample, which is the case at \( B \geq 0.5 \text{ T} \) for field cooled samples.

In the case of hard antiferromagnetic materials like the uranium-pnictides, however, one needs a very high field to obtain a sizeable magnetization at all. For UAs, a ferrimagnetic phase can be reached in a field of \( 10 \text{ T} \) (sec. 4.5). For UP, however, the magnetization and hence the Kerr-rotation is rather small even in a field of \( 10 \text{ T} \). Fig. 15 shows the temperature dependence of \( \theta_K \), which exhibits two first order phase transitions at 121 K and 21 K in excellent agreement with magnetization [37] and resistivity [72] measurements. The magnetic structure is only known for \( T \leq 21 \text{ K} \) to be antiferromagnetic type I for applied fields up to \( 13 \text{ T} \) [37].

![Fig. 15: Temperature dependent polar Kerr-rotation of cleaved UP at \( B=10 \text{ T} \) and \( h\omega=1.85 \text{ eV} \).](image-url)
In a field of 10 T, the magnetization of USb is even lower than in UP be-
cause no magnetic phase transition occurs. Instead of USb, we have there-
fore investigated the pseudo-binary compound USb0.85Te0.15 which
shows a ferromagnetic spin structure in a field of 6 T [34]. The magnetic
and crystallographic parameters of importance for the understanding of
the magneto-optical response for the investigated uranium-chalcogenides
and pnictides are summarized in tab. 3.

<table>
<thead>
<tr>
<th></th>
<th>US</th>
<th>USe</th>
<th>UTe</th>
<th>UP</th>
<th>UAs</th>
<th>USb 0.85 Te 0.15</th>
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</thead>
<tbody>
<tr>
<td>a [Å]</td>
<td>5.488</td>
<td>5.74</td>
<td>6.155</td>
<td>5.589</td>
<td>5.767</td>
<td>6.197</td>
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<tr>
<td>N [10²² cm⁻³]</td>
<td>2.42</td>
<td>2.11</td>
<td>1.71</td>
<td>2.29</td>
<td>2.08</td>
<td>1.68</td>
</tr>
<tr>
<td>μₜot [μₜ]</td>
<td>1.55</td>
<td>1.8</td>
<td>1.9</td>
<td>0.16</td>
<td>0.42</td>
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<td>&lt;111&gt;</td>
<td>&lt;100&gt;</td>
<td>&lt;110&gt;</td>
<td>&lt;111&gt;</td>
</tr>
<tr>
<td>μₙ [μₐ]</td>
<td>1.7</td>
<td>2.0</td>
<td>2.25</td>
<td>1.70</td>
<td>2.25</td>
<td>2.8</td>
</tr>
</tbody>
</table>

Tab. 3: Crystallographic [46] and magnetic data [34, 37, 40, 57, 73] for
uranium-chalcogenides and pnictides. N is the number of molecu-
les per cm³ and a is the lattice constant. The values displayed
in the last three columns refer to the conditions of the magne-
to-optical measurement displayed in fig. 16.

The energy dependence of the complex polar Kerr-effect for (100)-cleaved
single crystals of uranium-chalcogenides and pnictides is displayed in
fig. 16. In the chalcogenide series, the shape of the Kerr-spectrum is
similar in the low energy part while at higher energies, one structure in
θₖ seems to disappear going from US to UTe. The magneto-optical respon-
ses in the pnictide series is similar too, apart of a shift of the spec-
trum to lower energies with heavier anions. For the quantitative dis-
cussion of the magneto-optical data, we have calculated σₓᵧ, which is dis-
played in fig. 17.
Fig. 16: Complex polar Kerr-effect of (100)-cleaved single crystals of uranium-chalcogenides and pnictides. In the case of the chalcogenides, the measurements have been performed at $B=4 \, \text{T}$ and $T=15 \, \text{K}$. 
Fig. 17: The real ($\sigma_{1xy}$) and imaginary ($\sigma_{2xy}$) part of the off-diagonal conductivity tensor element for the uranium-chalcogenides and pnictides as computed from the Kerr-effect and the optical constants. The dashed line displays the extrapolation of $\sigma_{1xy}$ for $\hbar\omega<0.5$ eV obtained by Kramers-Kronig inversion. The solid and dash-dotted curves show the estimated free-electron contribution to $\sigma_{2xy}$ and $\sigma_{1xy}$, respectively. Note the different ordinate scales.
4.3.2.1 Spin-Polarization of Conduction Electrons

The "diamagnetic" line shape of the lowest energy transition (peak A) in \( \sigma_{xy} \) has already been established for UAs\(_x\)Se\(_{1-x}\) in sec. 4.2.2.2. The same argument of equal transition energies in \( \sigma_{xx} \) and \( \sigma_{xy} \) (at conditions, where magnetic energy shifts are negligible) leads to the conclusion, that the f-d transition has the same line shape in all six compounds and allows the estimation of the free electron contribution to \( \sigma_{xy} \) using eq. (8). The result is shown in fig. 17 as the dashed (\( \sigma_{2xy} \)) and dashdotted (\( \sigma_{1xy} \)) lines. The most important result of this analysis of course is, that the spin-polarization is negative for all six compounds, i.e. the number of electrons with antiparallel spin moment compared to the total magnetic moment exceeds the number of those with parallel spin moment. In addition, the sign of \( \sigma_{1xy} \) at \( \omega=0 \) predicts that all six materials should exhibit the same sign of the anomalous Hall-effect (eq. (6)), which has in fact recently been observed [72, 74].

In a second step, the size of \( \sigma_d \) may be estimated. The spin orbit factor \( P_0/ev_0 \) (eq. (10)) increases slightly from \( 1.95\times10^{-16}\) sec in US to \( 3.3\times10^{-16}\) sec in UTe and \( 2.1\times10^{-16}\) sec in UP to \( 3.4\times10^{-16}\) sec in USb\(_{0.85}\)Te\(_{0.15}\) due to the different energies of the f-d transition. Putting these numbers into eq. (8), the product of spin-polarization (in %) with the number of conduction electrons per uranium amounts to -0.46, -0.44 and -0.24 in the chalcogenide series and -0.06, -0.12 and -0.17 in the investigated pnictide series. Due to the small number of free electrons in USb\(_{0.85}\)Te\(_{0.15}\), the estimated amplitude of the conduction electron curves for this compound (fig. 17) should only be taken as an upper limit.

From the atomic configurations of uranium and the chalcogenides the number of conduction electrons per uranium \( n \) is expected to be between 1 and 2. A recent calculation [75] predicts a ground state close to \( f^3 \) in the chalcogenides and a fit of the optical reflectivity and \( \sigma_{xx} \) for US results in 1.1 d electrons per uranium [59]. Taking this value for \( n \), the size of \( \sigma_d \) comes out to be \( \approx -40\% \) in US and \( \approx -35\% \) in USe but only \( \approx -20\% \) in UTe. This result is in favorable agreement with spin-polarized photoemission experiments [76], which have shown the same sign and approximate size of \( \sigma_d \) and in particular the reduced \( \sigma_d \) for UTe. The microscopic origin of this reduction will be discussed in sec. 4.4 in the framework of a f-d band model for the explanation of magnetic red- and blue-shifts in USb\(_x\)Te\(_{1-x}\).
For uranium monopnictides the number of conduction electrons per uranium is expected to be between 0 and 1. A fit of the optical data results in about 0.45, 0.35 and 0.2 e-/U for UP, UAs and USb0.85Te0.15, respectively. However, these numbers can only be taken as a crude estimate because of the reduced energy range of the reflectivity measurements (the lower limit for the pnictides was 0.03 eV instead of 0.001 eV for US [46, 77] and USe [12]) and the obvious deviations from Drude behavior. On the other hand, in a recent interpretation of transport properties of the uranium pnictides similar numbers are postulated [72]. Taking therefore the values cited above, the spin-polarization for the field and temperature conditions mentioned in fig. 17 is found to be -15%, -30% and -100% for UP, UAs and USb0.85Te0.15, respectively. In other words, the local spin-polarization (sec. 4.2.2.2) amounts to -100% in all uranium pnictides, i.e. only one spin-polarized d subband is occupied.

4.3.2.2 The f+d Transition

The subtraction of the conduction electron contribution from the measured \( \sigma_{xy} \) results in the pure interband signal. It is obvious from fig. 17, that the lowest energy interband transition around 1 eV exhibits a 'diamagnetic' line shape in all six compounds and is therefore clearly identified as an f+d excitation (see also sec. 4.2.2.3). Table 4 lists the

<table>
<thead>
<tr>
<th></th>
<th>US</th>
<th>USe</th>
<th>UTe</th>
<th>UP</th>
<th>UAs</th>
<th>USb0.85Te0.15</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \hbar \omega_A \pm 2% \ [eV] )</td>
<td>1.13</td>
<td>0.94</td>
<td>0.77</td>
<td>0.78</td>
<td>0.82</td>
<td>0.65</td>
</tr>
<tr>
<td>( \langle \sigma_{xy} \rangle ) \ [10^{30} \text{ sec}^{-2}] )</td>
<td>10</td>
<td>9.4</td>
<td>5.0</td>
<td>1.2</td>
<td>2.3</td>
<td>16</td>
</tr>
<tr>
<td>( \langle \sigma_{xy} \rangle / N \mu_{tot} ) \ [10^{7} \text{ sec}^{-2} \text{cm}^{-3} \mu_B^{-1}] )</td>
<td>2.7</td>
<td>2.5</td>
<td>1.5</td>
<td>2.9</td>
<td>2.6</td>
<td>3.3</td>
</tr>
</tbody>
</table>

Tab. 4: Observed transition energy in \( \sigma_{xy} \), total weight \( \langle \sigma_{xy} \rangle \) and normalized off-diagonal oscillator strength \( \langle \sigma_{xy} \rangle / N \mu_{tot} \) of the f+d transition in the uranium-chalcogenides and -pnictides. The field and temperature conditions are mentioned in fig. 17. The approximate errors for \( \langle \sigma_{xy} \rangle \) and \( \langle \sigma_{xy} \rangle / N \mu_{tot} \) are \( \pm 10\% \) and \( \pm 15\% \), respectively.
energy, the total weight and the normalized off-diagonal oscillator strength of the f-d transition for the six investigated compounds. The transition energy decreases slightly along the chalcogenides and pnictides series but the width of the peak in $\sigma_{xx}$ remains nearly constant. Hence, the trends in $\sigma_{xy}$ corroborate the results of the Lorentz-fit of $\sigma_{xx}$ (tab. 2), presented in sec. 4.3.1.

A comparison of $\langle \sigma_{xy} \rangle$ and the total magnetic moment at measuring conditions indicates, that $f_{xy} = \langle \sigma_{xy} \rangle/N = \mu_{tot}$, i.e. the off-diagonal oscillator strength normalized to magnetization is approximately the same along the chalcogenides and pnictides series except for UTe. In detail, the experimental diagonal (tab. 2) and off-diagonal (tab. 4) total weights are expressed for these five compounds by the simple equations:

$$\langle \sigma_{xx} \rangle = 3.3 \cdot 10^{30} \cdot N \ [\text{sec}^{-2}]$$

$$\langle \sigma_{xy} \rangle = 2.8 \cdot 10^{29} \cdot N \cdot \mu_{tot} \ [\text{sec}^{-2}]$$

where the units of $N$ and $\mu_{tot}$ are $10^{-22} \text{ cm}^{-3}$ and $\mu_B$, respectively.

To explain these values, we propose the modified atomic model mentioned in sec. 3.2, which has been successfully applied for Gd [27] and the Europium-chalcogenides [8]. The dipole matrix element is evaluated in the approximation of atomic f and d wavefunctions to be $|\langle b|\vec{r}|a\rangle|^2 = 3R_{df}^2 = 2 \cdot 10^{-16} \text{ cm}^2$ for US, using the LMTO overlap integral calculated by Brooks [69]. Taking this value for the matrix element, eq. (16) reproduces the measured $\langle \sigma_{xx} \rangle$ if we assume an occupation of 1.4 f states. This number has to be viewed as an 'optical' occupancy which is expected to be less than the real occupancy in the case of correlated states [63]. Thus, the deviation from the expected number of 2.5 - 3 f electrons may be interpreted in terms of nonvanishing correlation effects which corroborates the model of a narrow f band in US.

One further interesting result may be obtained, if the integration in eq. (16) is dropped. In this case, the expression for the absorptive diagonal conductivity becomes

$$\sigma_{1xx} = \frac{\pi Ne^2}{\hbar} \sum_{\alpha\beta} |M_{xx}|^2 \int J_{\alpha\beta}$$

where $J_{\alpha\beta}$ is the joint density of states in units of states per eV.
This equation indicates, that the width of $J_{\alpha\beta}$ which is given approximately by the sum of the $d$ and $f$ band widths, is equal to the width $\Gamma_{xy}$ of $\sigma_{xx}$ for the $f+d$ transition. The experimental value (Fig. 14 and Tab. 2) is about 1.1 eV in all UX and UZ compounds. A comparison with similar materials like UO$_2$ and EuS indicates, that the $d$ width is expected to be $>1$ eV, i.e. the $f$ band width does certainly not exceed a few tenth of an eV for the uranium-monochalcogenides and monopnictides.

The theoretical expressions eqs. (12) and (16) for the diagonal and off-diagonal weights can be combined giving:

$$\frac{\langle \sigma_{xy} \rangle}{\langle \sigma_{xx} \rangle} = \sigma_f \sum \frac{(\omega_{\alpha\beta} - |\langle \beta|x-iy|\alpha \rangle|^2 - \omega_{\alpha\beta} + |\langle \beta|x+iy|\alpha \rangle|^2)/2}{\omega_{\alpha\beta} + |\langle \beta|f|\alpha \rangle|^2} \quad (22)$$

i.e. the ratio of $\langle \sigma_{xy} \rangle$ and $\langle \sigma_{xx} \rangle$ only depends on the orbital parts of the matrix elements and the joint spin-polarization of the initial and final state. In the framework of the microscopic model presented in sec. 3.2, the difference $\sum (\omega_{\alpha\beta} - |\langle \beta|x-iy|\alpha \rangle|^2 - \omega_{\alpha\beta} + |\langle \beta|x+iy|\alpha \rangle|^2)/2$ is evaluated to be $\approx 0.63 \ \text{R}_{df}^2$ using the atomic spin orbit parameters $\zeta_f=0.18$ eV and $\zeta_d=0.15$ eV [70]. Taking a width of 1 eV for the $f+d$ transition, the model predicts

$$\frac{\langle \sigma_{xy} \rangle}{\langle \sigma_{xx} \rangle} \approx 0.21 \ \sigma_f \quad (24)$$

The experimental value of this ratio for all investigated UX$_x$Z$_{1-x}$ compounds except UTe is given by eq. (20) to be about 0.085 $\mu_{\text{LO}}$. Thus, the $f$ spin-polarization comes out to be $\approx 60\%$ in US and increases with heavier anion to reach 100% in USb$_{0.85}$Te$_{0.15}$ of course within the assumption, that the spin-orbit parameters are the same for all compounds.

Apart from the spin-polarization and the energy and width of the $f$ states, the combination of optics and magneto-optics provides additional information about the symmetry of $f$ and $d$ states. If electronic wavefunctions are subject of a crystalline electric field, the degeneracy of states will be lifted according to the crystal symmetry. In the case of $d$ orbitals in a NaCl-type lattice, two energy levels with $t_{2g}$ and $e_g$ symmetry are expected which leads in general to a double structure of the
f+d transition. The size of the t2g - eg energy separation is expected from a simple point charge model to be ≈1.5-3 eV. Such a double structure has in fact been observed in many compounds like the Eu- and Tm-chalcogenides and UO2 with an experimental t2g - eg separation of about 2 eV. In the case of the investigated uranium compounds, however, the magneto-optical results (fig. 16) clearly evidence the existence of only one f+d structure, located around 1 eV, in the energy range up to 5.7 eV. The argument of a second transition beyond the upper limit of our measurement seems to be unphysical because it implies a crystal field splitting exceeding 5 eV. Especially for compounds with a large lattice constant this value is by far out of the expected range. On the other hand, a crystal field splitting in the order of 3 eV for the d states is observed in the p+d excitation spectrum for e.g. US [46] and band structure calculations find a value of ≈3 eV for US [44]. Thus it seems to be appropriate to interpret the absence of the f+d eg transition as an effect of selection rules between crystal field split f and d states. Fig. 18 schematically indicates by arrows the allowed transitions between all possible crystal field levels at the T-point [78]. At the right side in this figure, the possible symmetries derived from f states are displayed. It becomes clear that only one f+d transition is expected if the occupied f level is of T2'-symmetry. Hence we propose from optical and magneto-optical spectroscopy, that the ground state of the f+d transition is of T2'-symmetry (or T71'-symmetry in the double-group notation, which includes the spin) in the six investigated compounds. In fact, various band structure calculations corroborate this finding [45, 65, 68, 79, 80].

![Fig. 18: Selection rules of optical dipole transitions at T for electronic states in a cubic crystal field [78].](image)
A further interesting feature of the f+d transition in uranium chalcogenides and pnictides is the difference of $T_{\omega_A}$ above and below the magnetic ordering temperature (tabs. 2 and 4). We find a red-shift of the whole f+d peak by 0.2 eV in UP and UAs, while for USB$_x$Te$_{1-x}$ a double structure appears with decreasing temperature. In the chalcogenide series, the magnetic red-shift is small for US and USE, but shows the opposite sign for UTe. Because of the extraordinary behavior of UTe and USB$_{0.85}$Te$_{0.15}$, we will study the f+d transition and its correlation to the magnetic and electronic structure for USB$_x$Te$_{1-x}$ in the next section. The behavior of UP and UAs, on the other hand, has already been discussed in sec. 4.2.2.3.

At the end of this section, some remarks should be made about the reduced magneto-optical response of UTe (tab. 4). Because $\sigma_{xy}$ of UTe shows no reduction compared with the other compounds (tab. 2), the anomaly of $\sigma_{xy}$ is certainly not due to a lower density of states. In addition it is improbable, that the f spin polarization is reduced by a factor of 2 because of the large ferromagnetic moment. Hence, the diminution of $\sigma_{xy}$ has to be the consequence of a modified matrix element, which in the framework of our model means, that the spin-orbit energy is reduced by a factor of 2.

The hypothesis of a ground state with critical conditions for UTe is corroborated by the observation, that the magneto-optical response of UTe can be twofold, depending on the sample. The Kerr-spectrum shown in fig. 16, which is reproduced in the 0-3 eV energy range on the right side of fig. 19 is of the kind which is similar to all other UX$_x$Z$_{1-x}$ compounds. The left part of fig. 19, however, which shows the magneto-optical spectrum for the second type of UTe, is very similar to the Kerr-effect of Tm-compounds [30]. The microscopic origins of these two characteristic spectra are well understood. While the first one is caused by an f+d interband transition, the second one is due to different plasma frequencies for right and left hand circularly polarized light and the interband transition is suppressed. The size of the Kerr-signal of 9° indicates, that this plasma edge splitting has the extraordinary magnitude of ~0.1 eV.

It is important to note, that the magnetic behavior of the sample volume probed by the Kerr-effect has been established by magneto-optics to be equal for the two types of UTe. In both cases, the ferromagnetic ordering temperature was found to be 104±2 K. Fig. 20 shows a magneto-optical hysteresis loop measurement $\theta_K(B)$ at 10 K for the second type of UTe,
Fig. 19: Polar Kerr-effect for the two different types of UTe samples at \(B=4\)T and \(T=15\)K. Right part: f+d interband transition; left part: plasma edge splitting.

Fig. 20: Magneto-optical determination of the magnetic hysteresis loop for the type of UTe, which shows the characteristic features of a plasma edge splitting.
which agrees perfectly with bulk magnetization measurements [81]. Thus we conclude, that the probed material was UTe in both cases. The characteristic differences may originate from slightly different lattice constants of the two samples, which cause drastically different f-d ground states. For the first type, the f electrons form a narrow band at \( E_F \) similar to the other UX compounds which results in a magneto-optical response typical for \( UX_xZ_{1-x} \) materials. The second type of UTe, however, may have a slightly larger lattice constant, inducing a mixed valent behavior of f-d electrons. This hypothesis is corroborated by the observation, that f+d transitions, which are clearly resolved in semiconducting \( \text{TmSe}_0.32\text{Te}_0.68 \), seem to be absent in mixed valent \( \text{TmSe}_0.32\text{Te}_0.68 \)-polished) [82]. However, the physical mechanism which suppresses the interband transition is not known yet. For a clarification of this interesting problem, the investigation of the f state properties in chemically enlarged UTe crystals are in preparation.

4.3.2.3 Excitations of p and d Electrons

Both in the series of uranium-chalcogenides and -pnictides one further dominant peak apart from the f+d transition around 1 eV is observed in \( \sigma_{xy} \) (fig. 17). But as we have pointed out in sec. 4.2.2.3, the microscopic origin is different for the chalcogenides and pnictides.

The center of the valence p-band in the former group of compounds is found from photoemission experiments at 5.0, 4.5 and 3.8 eV binding energy for US, USe and UTe, respectively [49, 54]. In addition, p+d transitions are known to contribute to \( \sigma_{xx} \) only at \( \hbar \omega > 4.5 \) eV [46]. Fig. 17 evidences, that the magneto-optical signal from p excitations in these materials is less than \( 1 \times 10^{14} \) sec\(^{-1} \) at magnetic saturation, if it is present at all. Hence, only d and f electrons can be the origin of peak B in fig. 17. In sec. 4.2.2.3 it has been argued from the characteristic decrease of the oscillator strength in the \( \text{UA}_{x}\text{Se}_{1-x} \) system that an interpretation in terms of an d+f transition is obvious. This model is corroborated by the strong decrease of the transition energy \( \hbar \omega \) and oscillator strengths \( f_{xx} \) and \( f_{xy} \) going from US to UTe (tab. 5), which excludes again an interpretation in terms of an second f+d transition. This decrease of \( f_{xx} \) as well as of \( f_{xy} \) by a factor of 5.5 from US to USe is a puzzling result. A reduction of d occupation can not account for this effect because the number of d electrons varies at maximum between 1
Tab. 5: Transition energy in $\sigma_{xy}$ and the diagonal and off-diagonal weights for the d+f transition in uranium-monochalcogenides. The experimental conditions are given in figs. 14 and 17.

<table>
<thead>
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<td>$\omega_B$ [eV]</td>
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<td>2.4±0.2</td>
<td>1.75±0.3</td>
</tr>
<tr>
<td>$&lt;\sigma_{xx}&gt;$ [sec$^{-2}$]</td>
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<td>5.4×10$^{30}$</td>
<td>2.1×10$^{30}$</td>
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<tr>
<td>$&lt;\sigma_{xy}&gt;$ [sec$^{-2}$]</td>
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<td>5.0×10$^{29}$</td>
<td>2.5×10$^{29}$</td>
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</tbody>
</table>

and 2 electrons per formula unit. Indeed, the intraband contributions to $\sigma_{xx}$ and $\sigma_{xy}$ (figs. 14 and 17) have a similar size along the chalcogenides series. The decrease in oscillator strength of the d+f transition, however, may be explained by an increasing localization of the final states. For strictly localized f-states, as in many rare earth compounds, no d+f transitions have been observed at all [63]. Thus the decrease of $f_{xx}$ and $f_{xy}$ from US to UTe points to a substantial localization of the f states for the compounds with heavier anions.

Of course, the d+f transition is present in the light uranium-pnictides too, but it is weakened by the lower d occupation, which has been evidenced for UAs in sec. 4.2.2.3. However, even in the off-diagonal conductivity, peak B is hardly resolved because of the strong overlap with the dominant transitions A and C (fig. 17).

Structure C in $\sigma_{xy}$ of the uranium-pnictides has about the same energy and similar relative weights in the three compounds. This dominant feature in the magneto-optical spectra is also resolved in the fit of $\sigma_{xx}$ around 3.5 eV (fig. 14). A comparison with the uranium-chalcogenides evidences, that this transition is a special feature of the pnictides. Its microscopic explanation is most probably the excitation of high orbital momentum states at the top of the valence band, as has been discussed for UAs$_x$Se$_{1-x}$ in sec. 4.2.2.3. Different band structure calculations find the p-band at 2.3±0.4 eV binding energy for the three materials [45, 47, 60, 75, 80], which is in good agreement with photoemission results on UAs and USb [49, 50, 52, 54].
4.3.3 Summary

In this section the variation of the magneto-optical spectrum along the chalcogenide and pnictide series have been discussed. The f states behave similar in all compounds except USb, which shows a fine structure in the f+d transition feature. This special aspect is discussed in detail in sec. 4.4. In the case of UTe, the f band width approaches a critical value which leads to a twofold magneto-optical behavior.

The conduction electrons are negatively spin-polarized in all six compounds. In the uranium-pnictides the size of the local spin-polarization $\sigma_d$ reaches -100% due to the small number of d electrons, while in the chalcogenides $\sigma_d$ decreases from US to UTe by a factor of 2.

In the uranium-pnictides a magnetic red-shift of the f+d transition energy in the order of 0.2 eV has been established. Together with the conduction electron polarization, this leads to the conclusion, that the f-moment is dominated by the orbital part.

Magneto-optical response of bonding d electrons has been observed only for uranium-pnictides which corroborates a similar f occupation in the chalcogenides and pnictides as it has been concluded from the f+d oscillator strength, i.e. mainly d and s electrons of uranium take part in bonding while the f occupation is near 3 in all compounds.

4.4 Magnetic Red-Shift in Uranium Compounds

We have pointed out in sec. 4.3.2.3, that the f+d transition energies measured above and below the magnetic ordering temperature do not coincidence (tabs. 2 and 4). Especially for the uranium pnictides, a red-shift in the order of 0.2 eV has been established, while in the case of UTe, a blue-shift of about 0.1 eV has been observed. This extraordinary magneto-optical effect is well known from some magnetic semiconductors [83] and has been interpreted by a coupling of the conduction band to inner shell f electrons.

4.4.1 The f-d Exchange Interaction

In 1962 Vonsovskii and Izyumov [84] proposed, that in a ferromagnetic metal the electrons move in spin-polarized subbands. These ideas have been extended to semiconductors, where the spin-dependent splitting of the
conduction band leads to a red-shift of the absorption edge \([9]\). In the so-called s-f or d-f model the total Hamiltonian is given by the following expression \([85]\)

\[
H = H_C + H_F + H_{df}
\]

(24)

where \(H_F\) describes the intra-f interactions and the conduction electron part \(H_C\) includes kinetic energy and Coulomb interaction terms. The two subsystems are coupled by a local (intra-atomic) exchange interaction \(H_{df}\)

\[
H_{df} = -J_{df} \sum_i \vec{s}_i \cdot \vec{S}_i
\]

(25)

with the intra-atomic d-f exchange constant \(J_{df}\). Instead of the f spin \(\vec{S}\), which is of course the appropriate description for the Eu-chalcogenides \((4f^7; 8S_7/2)\), the total f momentum should be used in eq. (25) for \(l \neq 0\) states, i.e. \(\vec{S}_i\) should be replaced by \((g-1)\vec{J}\) where \(\vec{J}\) is the total angular momentum and \(g\) the Landé factor \([86]\).

In the framework of this theory \([85,87]\) the energy of the conduction band center for the t-spin direction is given in the approximation of small exchange \((J_{df} \ll 1 \text{ eV})\) by

\[
T^+ = T_0 - J_{df} s^+ \langle S^2 \rangle + I \langle n^+_t \rangle + \ldots
\]

(26)

In this equation \(T_0\) is the undisturbed d band center, \(\langle S^2 \rangle\) is the magnetization of the f system, \(I\) means the intra-atomic d-d Coulomb matrix element and \(\langle n^+_t \rangle\) is the d band occupation with opposite spin. For the other spin direction, the sign of the second term on the right side of eq. (26) has to be changed. The maximum shift of the f-d transition in the case of an empty d^+_t-band is given by eq. (26) to be

\[
J_{df} \langle S^2 \rangle_{\text{max}} / 2
\]

(27)

and it is reduced if \(\langle n^+_t \rangle \neq 0\).

In a more general treatment of d-f exchange \([85,87]\), i.e. without restricting the size of \(J_{df}\), the conduction band is shown to split into six subbands for each spin direction. Of course these quasiparticle...
levels show a large overlap for small values of $J_{df}$ thus approaching the two subband approximation. However, the interesting point of this generalized analysis is, that the spectral weights ('reduced density of states') of the subbands variate extremely if $\langle s^2 \rangle$ approaches saturation magnetization $M_0$, i.e. although the d band center does not show any appreciable shift at high magnetizations, new peaks may appear. In fact, this effect has been observed for EuS in the magnetization range between 0.9$M_0$ and $M_0$ [88].

It is obvious from the previous theory, that large red-shifts are expected only for ferromagnets and perhaps ferrimagnets. In the case of antiferromagnets, however, a small blue-shift of the f+d energy is the common behavior although some materials are known which also display a small red-shift [83]. The decisive factor is the spin structure of the antiferromagnet which determines sign and magnitude of the local magnetic exchange energy [89]. But compared to ferromagnets, the size of the shift is expected to be much smaller.

Finally it should be mentioned that the temperature dependence of the f+d transition energy follows the short range spin correlation function as it has been shown quantitatively by Rys et al [86]. In high fields or at low temperatures, however, spin-correlation function and Brillouin function will be similar.

4.4.2 The Pseudo-Binary System USbxTe1-x

As we have mentioned in sec. 4.3.2.2, red-shifts of the same size have been observed both in ferromagnetic USb$_{0.85}$Te$_{0.15}$ and ferri-(antiferro-)magnetic UAs and UP. We conclude further from the results presented up to now, that the sign of the magnetic shift must change in the system USbxTe$_{1-x}$ because for UTe, a blue shift has been established.

To study these different aspects of the f+d transition we have intensively investigated the system USbxTe$_{1-x}$. In zero field, compounds with $x<0.82$ are ferromagnets, while for $x>0.82$ ferri- or antiferromagnetic ordering occurs [38]. The magnetic parameters of the investigated compositions are summarized in tab. 6. The lattice parameter is nearly constant throughout the series.
Tab. 6: Magnetic parameters in the system \( \text{USb}_x \text{Te}_{1-x} \): ordering temperature \( T_N \) or \( T_C \) [38]; magnetization moment in the easy direction \( \mu_{\text{tot}} \) [38,81,90]; neutron moment \( \mu_n \) [34,90].

<table>
<thead>
<tr>
<th>( x )</th>
<th>0.9</th>
<th>0.85</th>
<th>0.8</th>
<th>0.5</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T_{C,N} ) [K]</td>
<td>205</td>
<td>204</td>
<td>204</td>
<td>201</td>
<td>102</td>
</tr>
<tr>
<td>( \mu_{\text{tot}} ) [( \mu_B )]</td>
<td>0.91</td>
<td>2.8</td>
<td>2.58</td>
<td>2.24</td>
<td>1.91</td>
</tr>
<tr>
<td>( B=4T; T=10K )</td>
<td>( B=6T; T=10K )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \mu_n ) [( \mu_B )]</td>
<td>2.8</td>
<td>2.8</td>
<td>2.64</td>
<td>-</td>
<td>2.25</td>
</tr>
</tbody>
</table>

4.4.2.1 Size of Red-Shift versus Type of Magnetic Order

We will demonstrate in this section, that the dependence of the magnetic red-shift on the type of magnetic ordering can be studied in the system \( \text{USb}_x \text{Te}_{1-x} \) without drastic changes of other parameters like the d occupation. Fig. 21 displays the Kerr-rotation in the f-d transition region.

![Fig. 21](image-url)
of ferrimagnetic USb₀.₉Te₀.₁ and ferromagnetic USb₀.₈₅Te₀.₁₅ at different temperatures. It is obvious, that the behavior of the f+d feature is similar in both compounds. Only the size of $\Theta_K$ reflects the by a factor of 4 higher magnetization in USb₀.₈₅Te₀.₁₅ compared to USb₀.₉Te₀.₁ whereas the shape and in particular the change of shape with temperature are nearly the same. In detail, the f+d transition shows a double structure in $\Theta_K$ even at $T\approx T_{\text{C, N}}$ and a transfer of oscillator strength from the higher energy part to lower energies with decreasing temperature is clearly observed. This behavior may be analyzed in detail in terms of the off-diagonal conductivity. Fig. 22 displays the absorptive, off-diagonal element, normalized to its maximum value, at four temperatures. It can be seen, that the f+d feature consists of one 'paramagnetic' peak around 1.5 eV and the dominant 'diamagnetic' structure at lower energies. While the latter one displays a red-shift of about 0.15

![Absorptive off-diagonal conductivity](image)

Fig. 22:
Absorptive off-diagonal conductivity of USb₀.₈₅Te₀.₁₅ at B=6 T and different temperatures. Each curve is normalized to its maximum value. For clarity, the spectra for $T=200$, $170$ and $10$ K are vertically shifted by 0.25, 0.5 and 0.75, respectively.
eV between 290K and 10K at B=6 T, the former structure shifts a little to higher energies with decreasing temperature. According to the theory (sec. 4.4.1), the shift of the f+d transition energy as a function of temperature should be proportional to the sample magnetization in high fields and at moderate temperatures. Fig. 23 shows a plot of $T_{\omega A}$, as determined from the peak energy in $\sigma_{xy}$, versus temperature for $\text{USb}_{0.9}\text{Te}_{0.1}$. In the same figure, the normalized magnetization from a bulk magnetization measurement is displayed [81]. The fit of $T_{\omega A}(T)$ is excellent and allows the determination of $T_{\omega A}(M=0)$ to be 0.85 eV which agrees favourably with the value from reflectivity measurements of $T_{\omega A}(M=0) = 0.87\pm0.02$ eV (tab. 2). By this way, the total shift for $\text{USb}_{0.85}\text{Te}_{0.15}$ and $\text{USb}_{0.9}\text{Te}_{0.1}$ is found to be 0.2\pm0.02 eV.

The observed temperature dependence of the f+d transition in $\sigma_{xy}$ for both uranium compounds exhibits strong similarities to the behavior of the europium chalcogenides [8]. For the latter materials the $f+nf^{n-1}d_{2g}$ feature in the Faraday-rotation shows four peaks due to an $f^{n-1}$ final state splitting [8]. Apart from a redistribution of oscillator strength for these structures with decreasing temperature, only the lowest energy

![Graph](image.jpg)

**Fig. 23:** f+d transition energy in $\sigma_{xy}$ versus temperature for $\text{USb}_{0.9}\text{Te}_{0.1}$ at B=4 T (dots) and normalized bulk magnetization $M/M_0$ (solid line) for the same field.
peak shifts to the red. This characteristic behavior which has its analogy in the Kerr-rotation \cite{91} is displayed in fig. 24 for EuSe in the ferromagnetic phase. While the red-shift for the discussed uranium-compounds is certainly caused by the d band, the origin of the double structure of the f+d transition may be either an initial or a final state effect. In the latter case, atomic splittings of the fn-1d configuration exceed the band broadening similar to the Eu-chalcogenides, i.e. this description leads to a picture of localized f electrons. The alternative to this view of the electronic structure are two transitions at different symmetry points in the Brillouin zone, which leads to a band description. Using the experimental data presented up to now, it is not possible to favour one of these models. However, the study of the whole system USb_xTe_{1-x} may give additional hints which perhaps allow the decision for one model because we know already from sec. 4.3.2.2, that within this series the
double structure for $x=0.85$ and 0.9 changes to a single structure for $x=0$.

It should be mentioned, that an interpretation of the double structure in terms of a Brillouin-zone doubling, which is well known for antiferromagnets, is improbable because the additional structure should vanish if the spins are alligned by a strong external field [92, 93]. Obviously, this does not happen in USb$_{0.85}$Te$_{0.15}$.

4.4.2.2 Localized versus Itinerant $f$ States in USbxTe$_{1-x}$

In the previous sections it has been demonstrated, that the $f$-$d$ energy shows a red-shift of about 0.2 eV in USb$_{0.9}$Te$_{0.1}$, while for UTe a blue-shift around 0.1 eV is observed. Thereupon we have measured the Kerr-rotation and ellipticity in the 0 - 3 eV energy range for several USbxTe$_{1-x}$ compounds at different temperatures. We have found, that the change from the double structure behavior in $\sigma_{xy}$ or $\sigma_{2xy}$ to a single peak occurs abruptly near $x=0.8$. Together with this change in shape, the sign of the shift alters. This behavior is visualized distinctly by a comparison of $\sigma_{2xy}$ at magnetic saturation for compounds with $x=0.85$ and 0.8 (fig. 25). While for zero magnetization, the $f$-$d$

![Fig. 25: Absorptive off-diagonal conductivity $\sigma_{2xy}$ normalized to its maximum values for the two compositions $x=0.85$ and 0.8 at magnetic saturation (B=6 T, T=10 K and B=4 T, T=10 K, respectively). For the former compound, zero is shifted vertically by 0.4.](image)
transition occurs at $0.86 \pm 0.02$ eV for both compounds, we find the resonance energy at magnetic saturation for the former compound at 0.65 eV but for the latter one at 0.95 eV. Hence, a change of the tellurium concentration by only 5% shifts the transition energy by as much as 50%.

Fig. 26 collects the observed total magnetic shifts in the system USb$_x$Te$_{1-x}$. While for $x<0.8$ the resonance energy increases with magnetization, it lowers for compositions with $x>0.8$. The abrupt jump at $x=0.8$ is corroborated by the fact, that samples with nominal composition $x=0.8$ exhibit different shifts from sample to sample.

The distinct spectra for the compounds $x=0.8$ and $x=0.85$ certainly reflect two drastically different f and d electronic densities of states. The change from the situation with higher f+d transition energy to the one with lower transition energy may also be generated by the application of pressure although the microscopic reasons may be different. Using the fact, that polishing of a surface may be equal to a pressure of 10-15 kbar [82, 94], Fig. 27a compares the Kerr-rotation at magnetic saturation of (100)- and (111)-polished USb$_{0.8}$Te$_{0.2}$ with the spectrum of a cleaved sample. In Fig. 27b, the normalized absorptive conductivity $\sigma_{2xy}$ for (100)-polished and -cleaved samples are displayed for the same temperature and field conditions. The comparison shows unequivocally, that due to the polishing treatment the f+d transition energy has shifted from 0.95
to 0.67eV. The low f+d energy for the polished sample agrees well with the one found for cleaved USb₀.₈Te₀.₂ (fig. 25) and the similarity of the corresponding $\sigma_{xy}$ spectra is obvious. However, there exists an important difference: while for cleaved USb₀.₈₅Te₀.₁₅ the f+d energy shifts with increasing magnetization from 0.85 to 0.65eV, this energy is nearly independent of magnetization for polished USb₀.₈Te₀.₂.

It should be noted in this context, that no substantial change of the f+d energy upon polishing has been observed for UAs and US (see fig. 1), i.e. the $dt_{2g}$ - $deg$ crystal field splitting seems not to increase substantially and therefore it is most probably not the driving mechanism for the lowering of the f+d transition energy upon polishing. This observation contrasts the experience with certain semiconductors [82, 94] certainly because of the partial occupation of the $dt_{2g}$ level in the uranium chalcogenides and pnictides.
A successful model of the electronic states in USbxTe1-x has to explain the following observations:

i) red- and blue shift in USb and UTe, respectively, with an abrupt change in sign at x=0.8;

ii) double structure of the f+d feature for x>0.8 and single structure for x<0.8;

iii) transition energies at zero magnetization (tab. 2) and at saturation magnetization (tab. 4);

iv) conduction electron spin-polarizations of -100% in USb0.85Te0.15 and only -20% in UTe.

v) pressure induced change of the f+d energy in USb0.8Te0.2.

In the following we will discuss the consequences for the model of f and d states which emerge from these observations both in a localized and an itinerant description of the f electrons.

Band model of f electrons: Within this model the occupied f-band approaches the Fermi-energy at certain symmetry points of the Brillouin zone (e.g. at L and Γ) whereas due to the strong pf hybridization it is pulled away from Ef e.g. at the X point. The d band in fcc symmetry [68], on the other hand, is lowest in energy at X and highest at the L-point within the L-Γ-X k-ray. The Fermi energy for USbxTe1-x compounds with x>0.8 is placed at the bottom of the d band, while it shifts to higher energies with decreasing x due to the successive filling of the d states. The f band, however, is pinned at Ef independently of x because the number of f electrons is approximately constant. The resulting bands near Ef for UTe and USb at room temperature are displayed by the solid lines in fig. 28a and 28b. The double structure for compounds with x>0.8 is explained by two transitions at the X and the L-point. The situation for the magnetized crystals, on the other hand, is displayed by the dashed lines in fig. 28, showing a red-shift of the transition at X and a blue-shift at L.

As soon as the Fermi-energy reaches some critical value in going from USb towards UTe, the f+d transition at X suddenly will become impossible because of an occupation of the final state, leaving only one f+d peak, which shows a blue-shift with magnetization (fig. 26).

This band structure model easily explains the conduction electron spin-polarization, too. Up to some value of Ef, it is -100% due to the filling of only the lower lying spin-polarized subband. Beyond this limit it begins to decrease rapidly because then, mainly the opposite spin direc-
Fig. 28: f and d bands in the vicinity of $E_F$ as proposed for the explanation of the magneto-optical data of the $\text{USbxTe}_{1-x}$ system. The dashed lines indicate the spin-polarized subbands at $T < T_{C,N}$. The arrows display the directions of the spin-moments for the f and d bands.

The proposed general behavior of the d and f bands near $E_F$ in the $\Gamma$-X and $\Gamma$-L directions is corroborated by several band structure calculations for UTe, UBi, UN and US [45, 68, 79, 80, 95]. A calculation for CeN [96], a material which shows very similar spectroscopic features as the discussed uranium compounds [97], corroborates the overall behavior of the f and d bands. This calculated band structure is in excellent agreement with the mentioned optical data.

We may resume, that the presented band scheme explains most of the experimental facts. However, an interpretation of the spectrum 'under pressure' and the explanation of the 'diamagnetic' line shape for the lowest energy transition for all compounds is lacking.

Model of localized f-states in USB: In this model, a localized-itinerant transition for the f states is proposed at $x=0.8$ in $\text{USbxTe}_{1-x}$ i.e.
the f$^3$ state is localized in USB and itinerant in UTe. The double structure of the f+d transition for compounds with x>0.8 is explained by a final state splitting of the f$^2$d$^1$ final state. In fact, a calculation of the coefficients of fractional parentages in intermediate coupling gives only two final state levels $^3$H$_u$ and $^3$F$_2$ with sufficient intensity and in addition, the lower energy level is calculated to be a factor of three more intensive [98]. The coupling of the 6d electron with the remaining 5f$^2$ state, which is known to be important for semiconductors [8, 10, 82], has been neglected in this calculation.

We assume, that the localized-itinerant transition at x=0.8 is triggered by the competition of the df-hybridization, which tends to keep the f level at $E_F$, and the pf-hybridization, which likes to pull the f-states below $E_F$. The trend of the f+d energy (fig. 33) to be highest in USB corroborates a model of localized f states in USB and is hardly in coincidence with localized states in UTe and non-localized ones in USB, as has been proposed from some photoemission data [54].

In the framework of this second model, good agreement with the finding of localized f states in USB by specific heat [48], transport [72] and neutron scattering [99] experiments is obtained. However, there is no obvious relation between the change of sign in the magnetic energy shift and the proposed localized-itinerant transition of the f states.

Hence we may conclude, that both models have serious shortcomings. In our opinion, however, the band model is the more unconstrained interpretation. Within this model, one may imagine also a low density of f states at $E_F$ if the f levels at the L and X-point are interpreted as two crystal field levels forming the f band. Then, the Fermi-energy is located just above the f state at L.

4.4.3 Discussion

In secs. 4.2 - 4.4, magnetic exchange induced variations of the f+d transition have been discussed for UP, UAs, UAs$_{0.7}$Se$_{0.3}$, USe and the system USB$_x$Te$_{1-x}$. In a first approach, this effect may be understood in the framework of the d-f exchange model, presented in sec. 4.4.1.

In the case of the uranumpnictides, the magneto-optical response evidences a -100% local conduction electron spin-polarization, i.e. only the subband with spin antiparallel to the total f-moment is occupied. Hence, the third term in eq. (26) vanishes and the f-d exchange constant may be calculated from eq. (27). However, the question arises, which value has
to be taken for the sublattice saturation moment $\langle S^2 \rangle$.

In the case of a free magnetic ion of total angular momentum $\vec{J}$, the saturation moment $\mu_{\text{sat}}$ and the paramagnetic moment $\mu_{\text{eff}}$ are given by $\mu_{\text{tot}} = gJ$ and $\mu_{\text{eff}} = g\sqrt{J(J+1)}$, respectively. However, this simple relationship breaks down for a solid, if strong crystal fields are present [100] which is obviously the case for the uranium chalcogenides and pnictides (fig. 5).

Because the actual angular momentum enters into the intra-atomic exchange Hamiltonian (eq. (25)), we will take $gJ$ from the measured paramagnetic moment $\mu_{\text{eff}}$ and not from the saturation moment $\mu_{\text{tot}}$ (see fig. 5). The paramagnetic moment is nearly constant for the pnictides and results in $gJ = 3.25 \mu_B$. Consequently, the f-d exchange parameter $J_{df}$ comes out to be about 0.12 eV for UP, UAs and USbxTe$_{1-x}$ with $x > 0.8$.

Going from the pnictides to the chalcogenides, the increasing occupation of the d band will reduce the red-shift, as predicted in the d-f model. Thus, the model is adequate for the application to the compounds with light anions, while in the case of USbxTe$_{1-x}$ the observed effects are determined by the band structure and therefore the simple model is overstressed.

It should be mentioned, that an interpretation of the observed magnetic changes of the f+d transition energy by magnetostriction is inadequate. Data of the lattice constant $a$ of UTe versus magnetization reveal a small decrease of $a$ in the order of $\Delta a/a = 1.5 \times 10^{-3}$ [101]. This value would lead via an increase of the d crystal field splitting to a red shift in the order of $< 0.01$ eV [102], i.e. it leads to a shift which has the opposite sign and which is one order of magnitude to small. In the case of UP [101], the experimental value of $\Delta a/a$ is lower by a factor of 30 compared to UTe and thus it can not explain the magneto-optical observations, too.

At this point of the discussion, some explanations should be given for the antiferromagnetic compounds regarding the so called 'local' conduction electron spin-polarization and the unexpected observation, that the size of the magnetic shift seems to be proportional to the sublattice magnetization while the Kerr-rotation itself is proportional to the bulk magnetization.

Let us consider an antiferromagnetic structure composed of ferromagnetic planes stacked e.g. in the sequence +++. Within these planes, the spin-polarized band structure equals that of a ferromagnet displayed in fig. 28. Along the $\vec{k}$-direction perpendicular to these planes, however, the spin-polarized subbands of $F$ and $d$ states have to cross each other to
achieve the antiferromagnetic ordering. The spin-polarized d and f densities of states for two adjacent planes with opposite total moment is visualized in fig. 29a. It becomes clear, that within each plane, the size of the magnetic shift is determined by the sublattice magnetization and the sign of the shift is the same in both sublattices for a f+d transition conserving the spin. This explanation holds as long, as the optical transitions do not occur at Brillouin-zone symmetries inbetween oppositely magnetized ferromagnetic planes. The sign of the Kerr-rotation, on the other hand, is of course opposite for the transitions in differently magnetized planes and therefore, $\theta_K$ sums to zero (fig. 29b). If a magnetic field is applied, $\theta_K$ will be proportional to the introduced net magnetization.

The same conclusion of course is valid for the magneto-optically determined conduction electron spin-polarization.

Hence we may conclude, that the observed optical transitions predominantly occur within the ferromagnetic planes for the uranium pnictides. This model explains in addition, that no additional transitions caused by a magnetic Brillouin-zone doubling can be expected because this doubling occurs only along the antiferromagnetic stacking direction.

The mentioned possibility of a magnetic red-shift for an antiferromagnetic material in zero applied field poses the question, how this effect in

![Figure 29](image)

Fig. 29: Sketch of the spin-polarized sublattice (a) and total (b) density of states for f and d electrons in the uranium pnictides. The arrows indicate the direction of the spin-moments.
general may be determined experimentally. The use of magneto-optics has the disadvantage to require relatively high applied fields to obtain a net magnetization. For zero field measurements, the determination of the optical reflectivity or the absorption constant would be appropriate, because these properties do not depend on the macroscopic moment.

Unfortunately, an easy measurement of the f+d absorption edge is impossible because of the metallic properties of all the uranium compounds. To get an idea, what are the expected differences for measurements above and below the magnetic ordering temperature, we have calculated the influence of a f+d red-shift on the reflectivity $R$ and the absorption constant $K$ for UAs. The solid lines in fig. 30 display the calculated spectra of $R$ and $K$ at room temperature obtained by a six oscillator fit of the measured $R$ up to 12 eV. The effect of a 0.2 eV red-shift of the f+d transition energy, keeping all other oscillators unchanged, is visualized by the dashed lines. The essential change in the reflectivity spectrum is a 5% increase in magnitude near $\hbar\omega_A$, indicating that the measurement of $R$ is certainly not straightforward for this purpose.

The direct determination of the absorption constant, i.e. the optical density of a thin film seems to be more appropriate as it becomes clear from fig. 30b. However, also in the optical density, the 0.2 eV shift of $\hbar\omega_A$ from 1.0 eV to 0.8 eV manifests itself in a modification of $K$ in the 0.5 - 2.5 eV energy range with varying horizontal shifts.

![Fig. 30: Calculated reflectivity (a) and absorption constant (b) of UAs, using an f+d transition energy of 1.0 eV (solid curves) and of 0.8 eV (dashed curves), respectively.](image)
4.5 Magnetic Phase Diagram of UAs

Among the UX-compounds, UAs is certainly the compound which exhibits the most complex magnetic behaviour [34]. To demonstrate magneto-optics as a powerful tool for the investigation of magnetic phase transitions, we have reexamined the magnetic phase diagram of UAs in applied fields up to 10T. In fig. 31 the computer graph of the measured temperature dependence of the Kerr-rotation is reproduced for a (001)-cleaved single crystal with the applied magnetic field along (100) as a parameter. Around \( T_N = 124.5\)K one observes at medium fields the appearance of an intermediate phase with higher magnetization than the surrounding paramagnetic and antiferromagnetic (type I) structures. This intermediate phase has been identified by neutron scattering to be single - \( \bar{k} \) ferrimagnetic with a (001) stacking of ferromagnetic planes [34]. The triple point of coexisting paramagnetic, antiferromagnetic and ferrimagnetic phases is found at \( B=3T \) and \( T=124.5\)K. For \( B < 9T \), fig. 31 exhibits at \( T = 62\)K the phase transition to the double-\( \bar{k} \) antiferromagnetic type IA structure. This transition is accompanied by a 10% decrease in magnetization which is due to the jump of the magnetic moments from a (001) to a (110) direction [34]. At \( B = 9.2T \) and \( T = 61.5\)K we find the triple point of two antiferromagnetic phases (type I and IA) and another ferrimagnetic phase with a double-\( \bar{k} \) structure. For comparison, the field-temperature plot from magnetization and neutron scattering experiments [34] is displayed in fig. 32.

Besides the described transitions, which have been observed on several cleaved UAs single crystals, one sample showed at 10T between 53K and 62K one further magnetic structure displaying a strong hysteresis as can be recognized in fig. 7c. The magnetic moment at 10T in this additional phase, which was also not found by neutron scattering in all investigated samples [34], is estimated from our magneto-optical data to be 0.53\( \mu_B/U \). This value corresponds to the magnetization expected theoretically for the 2k-ferrimagnetic structure [34]. The reduced experimental value of 0.42\( \mu_B/U \) found for \( T<53\)K is explained [34] by defects in the stacking sequence of ferromagnetic sheets. The introduction of stacking defects is accompanied by a change in magnetization but the wave vector remains unchanged in agreement with the neutron experiments. The observation of the same size of the Kerr-rotation for both kinds of UAs crystals at 10T and \( T<40K \) indicates that only the crystals with the additional
Fig. 31: Temperature dependence of $\theta_K$ measured on a cleaved UAs single crystal in fields up to 10 T and decreasing temperature. Consecutive curves are shifted by 0.1° for clarity.

Fig. 32: The magnetic phase diagram of UAs as derived from magnetization and neutron scattering experiments [34].
phase between 54K and 62K at 10T possess a $2\pi$ ferrimagnetic structure without stacking faults. Our observation of dramatic changes of the magnetic phase diagram on polishing (fig. 7c) suggests that also the different magnetic behaviour of the two kinds of UAs single crystals reflects the large sensitivity of the magnetic properties of this material to internal strain and stress.

In fig. 7c we have added the field cooled temperature dependence of $\Theta_K$ at 10 T measured on a polished surface. We observe, that $T_N$ as well as the size of the rotation in the ferrimagnetic phases remain unchanged compared with the cleaved sample, but $\Theta_K$ (or the magnetization) increases quite strongly in the antiferromagnetic and paramagnetic regions. These changes of the magnetic phase diagram have to be related to the deformation of the regular lattice by the polishing process. Phase transitions from the semiconducting to the metallic state in certain semiconductors, which need about 6-15kbar hydrostatic pressure, are known to occur also on polishing [82, 94]. On the other hand magnetization measurements at hydrostatic pressure in fields up to 7T on UAs have shown that only minor variations of the transition temperatures occur up to 8kbar [103] whereas the magnetization of the antiferromagnetic phases was shown to be independent of pressure. Thus in the case of UAs the effect of polishing can not simply be correlated with the application of hydrostatic pressure but more complicated phenomena such as alterations of exchange energies have to be evoked.

5. THE VALENCE OF URANIUM IN U$_x$Y$_{1-x}$Sb

5.1 Introduction

In the uranium pnictide series, the spatial overlap of the 5f wavefunctions decreases with increasing size of the anion. However, due to strong crystal field and hybridization effects, the f-states form a narrow band even in USb as we have recognized in the last chapter. Diluting the uranium sublattice in USb by nonmagnetic ions like Th or Y further increases the spatial separation of the magnetic ions and thus perhaps provides the possibility to study an increasing localization of the 5f electrons. Dilution with trivalent yttrium having the atomic configuration 3d$^1$4s$^2$
decreases the total number of 5f electrons whereas the d occupation remains nearly unchanged. Dilution with thorium, on the other hand, varies the number of both the 5f and 6d electrons due to the atomic configuration [Rn]6d27s2 of Th. Therefore, the former way is the appropriate method for the study of the pure effect of spatial separation on the f band and to check the band structure proposed for USb in the last chapter. A second stimulation for the magneto-optical study of the pseudo-binary system \( U_xY_{1-x}Sb \) is the interpretation of electrical resistivity, optical, magnetic and lattice constant data in terms of a valence transition [11] from a localized 5f2 state for \( x<0.15 \) to an intermediate valent \( 5f^{3-n} \) state for \( x>0.15 \). In particular, magneto-optics may allow the determination of the \( f^3+2d \) transition energy \( \hbar \omega_A \) as a function of \( x \) with a much higher resolution compared to the normal reflectivity and thus may check the major conclusion from the optical data of a continuous decrease of \( \hbar \omega_A \) with decreasing \( x \) down to \( \hbar \omega_A=0 \) at \( x=0.15 \).

The physical properties of this system are quite well investigated. For all compositions \( x \), a metallic conductivity is reported [11]. The magnetic order [34] is of type I antiferromagnetism with a triple-\( \bar{k} \) structure down to \( x=0.55 \) and changes at this composition directly to ferromagnetism. At concentrations below \( x=0.2 \) a paramagnetic behavior has been observed [34].

### 5.2 Results and Discussion

We have investigated magneto-optically the three compositions \( x=0.7, 0.4 \) and 0.15 of \( U_xY_{1-x}Sb \). The temperature dependences of \( \Theta_K \) indicate for the three compounds an antiferromagnetic, ferromagnetic and paramagnetic behavior, respectively, as it is expected from the magnetic data collected in tab. 7.

<table>
<thead>
<tr>
<th></th>
<th>0.7</th>
<th>0.4</th>
<th>0.15</th>
</tr>
</thead>
<tbody>
<tr>
<td>magnetic order</td>
<td>AF I</td>
<td>F</td>
<td>P</td>
</tr>
<tr>
<td>( T_{C,N} ) [K]</td>
<td>181</td>
<td>102</td>
<td>0</td>
</tr>
<tr>
<td>( \mu_{\text{tot}} ) [( \mu_B )/U]</td>
<td>0.7</td>
<td>1.71</td>
<td>0.34</td>
</tr>
<tr>
<td></td>
<td>B=7T; T=181K</td>
<td>B=4T; T=10K</td>
<td>B=7T; T=10K</td>
</tr>
</tbody>
</table>

Tab. 7: Magnetic data of the investigated \( U_xY_{1-x}Sb \) compounds [34, 81].
The energy dependence of the complex Kerr-effect, displayed in fig. 33, shows for all three compounds a sharply structured behavior at the low energy side of the spectrum, similar to all other uranium chalcogenides and pnictides. With increasing substitution of U by Y, this f+d feature narrows substantially. Fig. 34 displays the off-diagonal conductivity as calculated from the Kerr-effect and the optical constants of ref. 11. Similar to the spectrum of USb$_{0.85}$Te$_{0.15}$ shown in fig. 17, we observe a double structure for the f+d transition with a 'diamagnetic' peak at the low energy side and a 'paramagnetic' structure at higher energies. The resolution of this two peaks becomes better with increasing dilution due to the narrowing of the two lines. In particular for U$_{0.15}$Y$_{0.85}$Sb, the two peaks are located at 0.5 and 1.2 eV, respectively, indicating that the f+d transition energy has not yet shifted to zero for x=0.15.

Fig. 35 compares the energy of the 'diamagnetic' structure in the two systems USb$_x$Te$_{1-x}$ and U$_x$Y$_{1-x}$Sb in the magnetically ordered and in the paramagnetic state. Obviously the transition energy is highest for USb and decreases towards UTe and YSb. However, the physical reasons of this drop are different in the two pseudo-binary systems. Going from UTe to USb, the d occupation is reduced by approximately 1 electron per formula unit which results in a reduction of the Fermi-energy. According to fig. 28, the f-states at the L-point are pinned at $\epsilon_F$ and thus $\Delta\omega_A$ increases. Going from USb to YSb, on the other hand, does not change $\epsilon_F$ relative to the d band. However, the reduction of $\Delta\omega_A$ in this series reflects the decreasing strength of pf-hybridization. According to fig. 28, the lowest energy f+d peak in U$_x$Y$_{1-x}$Sb corresponds to a transition at the X-point. Compared to a hypothetical energy level scheme without pf hybridization, the f level is pulled away from $\epsilon_F$ due to the interaction with p wavefunctions, while the p band is pushed towards $\epsilon_F$. Diluting Y in USb now has the same effect as pushing down the valence band because the energy gained from pf-mixing decreases. Consequently the f states move closer to the Fermi-level. Such an effect has already been inferred for diluted CeSb [104].

Hence we conclude, that the band structure proposed for USb in fig. 28 still holds for U$_x$Y$_{1-x}$Sb but with a decreasing f binding energy at X with dilution. This interpretation is in agreement with an UPS-result on U$_{0.5}$Y$_{0.5}$Sb, finding the same shape of the energy distribution curve as for USb [54]. The conclusion of a vanishing $\Delta\omega_A$ at x=0.15 drawn from the diagonal conductivity [11], on the other hand, appears to be incorrect.
Fig. 33: Energy dependent polar Kerr-rotation and ellipticity of (100)-cleaved single crystals of $U_xY_{1-x}$Sb with $x=0.7$, 0.4 and 0.15. Note the different ordinate scales and the expanded energy scale for $x=0.15$.

Fig. 34: Absorptive ($\sigma_{2xy}$) and dispersive ($\sigma_{1xy}$) part of the off-diagonal conductivity for the three $U_xY_{1-x}$Sb compounds. The dashed line displays the extrapolation of $\sigma_{xy}$ for $\hbar\omega$$<0.5$eV obtained by Kramers-Kronig inversion (sec. 3.1). Note the different ordinate scales and the expanded energy scale for $x=0.15$. 
Fig. 35: Energy of the 'diamagnetic' part of the f+d transition in the pseudo-binary systems USbxTe1-x and UxY1-xSb in the magnetically ordered and disordered state, respectively. The open circle displays the f+d energy for polished USb0.8Te0.2 (sec. 4.4.2.2).

It is not surprising, that the f+d transition has not been detected unambiguously in the diagonal conductivity for compounds with x<0.15 because its amplitude in $\sigma_{1xx}$ for U0.15Y0.85Sb is only 15% of the amplitude in USb, i.e. it amounts to only $0.3 \times 10^{15}$ sec$^{-1}$. In general a signal of this size is hardly resolved in the optical reflectivity at low energies because of the dominating conduction electron contribution (even if the number of free electrons is small) and the overlap with strong valence band contributions in the refractive index. This situation in $U_xY_{1-x}Sb$ is a nice example to demonstrate the superiority of magneto-optics for the identification of weak excitations of magnetic electrons. With the knowledge of $\hbar \omega_A=0.55$ eV for the f+d transition in U0.15Y0.85Sb from the magneto-optical spectra, the corresponding peak in $\sigma_{1xx}$ of ref. 11 can easily be identified.

The high energy structure of the f+d transition around 1.25eV is well resolved in the magneto-optical spectra of the three $U_xY_{1-x}Sb$ compounds and compares well with the same feature in USb0.85Te0.15. According
to the energy level scheme for USb (fig. 28), it is attributed to an f+d transition at the L-point. In the diagonal conductivity of ref. 11 for the compounds with small uranium concentration, we find a weak shoulder at an energy of 1.25 eV, too, while this structure is lost in the high background for compounds with $x>0.3$ [11].

The total weight of the whole f+d transition in $U_xY_{1-x}Sb$ is found to be roughly proportional to the magnetic moment and the uranium concentration. This result again makes a valence transition in the composition range $x>0.15$ very unlikely.

The main result of the present magneto-optical study is, that the proposed itinerant model for the f states in $USb_Te_{1-x}$ with an occupation slightly less than three works also to explain the magneto-optical behavior for all investigated compositions of $U_xY_{1-x}Sb$. Within this model, the f+d transition consists of two excitations at the X and L points in the Brillouin-zone. The main influence of the dilution of the magnetic ion is a reduction of the pf-mixing at the X-point which results in a decrease of the f+d transition energy down to 0.5 eV in $U_{0.15}Y_{0.85}Sb$. Thus, the present results strongly support an f occupation near three down to a dilution of $x=0.15$. 
6. THE TERNARY COMPOUNDS UAsSe AND ThAsSe

6.1 Introduction

In the last two sections an comprehensive magneto-optical study of rock-salt-structure uranium compounds has been presented regarding the density of states a few eV around $E_f$, the f-d exchange and the spin-polarization of these states. The f electrons are found to be almost itinerant with a band occupation near 3. Due to this itinerant behavior, the f-d transition exhibits large diagonal and off-diagonal oscillator strengths and shows a simple 'diamagnetic' line-shape in the magneto-optical spectrum. On the other hand, the magneto-optical response of the localized 5f$^2$ state of UO$_2$ displays a pronounced final state splitting of the f-d feature into two structures separated by $\approx$1 eV [10]. This double structure indicates a strong interaction of the excited electron with the remaining 5f$^{n-1}$ state and in fact the spectrum is understood perfectly by atomic theory treating the 5f$^1$6d$^1$ excited state in UO$_2$ as a whole. Of course now the question raises, whether metallic uranium compounds exist, for which the magnetic f electrons are localized in a 5f$^2$ or a 5f$^3$ configuration. This situation may be present in the ternary compounds UZX (and also UZ$_2$) with Z=P, As, Sb and X=S, Se, Te, which are reported to have a localized 5f$^2$ magnetic ground state from magnetic data [105], photoemission data [106, 107] and by crystallographic considerations [108]. These proposals have stimulated the optical and magneto-optical investigation of UAsSe and the isostructural compound ThAsSe, which are presented in the following.

Both materials crystallize in the tetragonal PbFCl crystal structure with similar lattice parameters a and c (UAsSe: $a=3.986\AA$, $c=8.384\AA$; ThAsSe: $a=4.081\AA$, $c=8.562\AA$ [108]). The PbFCl structure is composed of layers of cation and anion, which in UAsSe, for instance, are stacked in the sequence As-U-Se-Se-U-As along the c-axis. A random distribution of As and Se atoms on the two different lattice sites has been excluded by neutron scattering and the investigation of UAs$_{2-x}$Se$_x$ solid solutions [109]. The crystallographic unit cell of the PbFCl structure is shown in fig. 36a and the coordination polyhedron around the uranium ion is displayed in fig. 36b. The distances between the cations and anions, marked in fig. 36b by $R_1$, are collected in tab. 8. For comparison, the inter-
Fig. 36: a) The crystallographic and magnetic unit cell of UAsSe and ThAsSe. Black circles: U or Th; small empty circles: As; large empty circles: Se.

b) The coordination around the uranium ion (black circle) in the PbFCl type crystal structure.

atomic distances for the rocksalt structure compound UAs are juxtaposed. The bonding conditions in these layered compounds are by far more complex than those of the NaCl structure because of the different interatomic distances (tab. 8). In particular, strong anion-anion bonds are suggested by the small As-As separation.

<table>
<thead>
<tr>
<th>atom neighbour</th>
<th>coordination number (PbFCl-structure)</th>
<th>distance (Å) UAsSe</th>
<th>distance in fig. 35</th>
</tr>
</thead>
<tbody>
<tr>
<td>U</td>
<td>4</td>
<td>3.986</td>
<td>R1</td>
</tr>
<tr>
<td>As</td>
<td>4</td>
<td>3.022</td>
<td>R2</td>
</tr>
<tr>
<td>Se I</td>
<td>4</td>
<td>3.937</td>
<td>R3</td>
</tr>
<tr>
<td>Se II</td>
<td>1</td>
<td>3.027</td>
<td>R4</td>
</tr>
<tr>
<td>As</td>
<td>4</td>
<td>2.818</td>
<td>R5</td>
</tr>
<tr>
<td>Se I</td>
<td>4</td>
<td>3.986</td>
<td>R6</td>
</tr>
<tr>
<td>Se I</td>
<td>4</td>
<td>2.969</td>
<td>R7</td>
</tr>
</tbody>
</table>

Tab. 8: Interatomic nearest neighbours distances in UAsSe [108, 109] and in UAs.
Magnetization [105] and neutron scattering [109] measurements have revealed ferromagnetic ordering in UAsSe below $T_C = 109$ K [110] with a saturation moment of $\mu_{\text{tot}} = 1.36 \mu_B$ and a neutron moment of $\mu_n = 1.5 \mu_B$. The magnetic structure is collinear with ferromagnetic layers perpendicular to the c-axis (fig. 36a). ThAsSe, on the other hand, is diamagnetic [108].

6.2 Results and Discussion

We have measured the room temperature reflectivity in the 0.03-12 eV energy range of UAsSe and ThAsSe. The measurements have been performed under high vacuum conditions on in situ cleaved single crystals. Details are described elsewhere [46].

For high energies, the reflectivity spectra (fig. 37) for both compounds are similar but they exhibit marked differences at $\hbar \omega < 4$ eV. While for ThAsSe the reflectivity curve shows a Drude behavior, a strong interband transition around 1 eV is observed for UAsSe similar to the uranium monopnictides and especially to UAs [46]. Using standard extrapolations at the low and high energy sides of the measurement [46], the spectra have been Kramers-Kronig transformed to derive the optical constants. The ab-

![Fig. 37: Near normal incidence reflectivities of UAsSe and ThAsSe cleaved single crystals at room temperature.](image)
The absorptive part of the diagonal conductivity for UAsSe and ThAsSe at room temperature is displayed in Fig. 38. It should be mentioned that the conductivity tensor may be written as in eq. (2) also for a tetragonal lattice, if the c-axis is perpendicular to the sample surface. But in contrast to cubic symmetry, $\sigma_{xx} \neq \sigma_{zz}$ even for $B=0$ because of the two different lattice parameters $a$ and $c$. For the configuration of light propagation parallel to the c-axis, the optical measurements probe the conductivity within planes perpendicular to the c-axis. To separate the 'magnetic' from the 'nonmagnetic' electrons, we have measured in addition the polar Kerr-rotation and ellipticity of UAsSe at magnetic saturation (Fig. 39a). The complex off-diagonal conductivity $\sigma_{xy}$, calculated by eq. (3) from the Kerr-effect and the optical constants is displayed in Fig. 39b. A comparison of the magneto-optical response $\sigma_{xy}$ for UAsSe and UAs (Fig. 17) again visualizes large similarities.
Fig. 39: a) Complex polar Kerr-effect of cleaved UAsSe at magnetic saturation (B=5 T and T=10 K).

b) Complex off-diagonal conductivity at magnetic saturation as calculated from the polar Kerr-effect and the optical constants. The extrapolation for \( \hbar \omega < 0.5 \) eV is estimated by Kramers-Kronig transformation (sec. 3.1).

6.2.1 f- and d-States

A comparison of \( \sigma_{xx} \) and \( \sigma_{xy} \) for UAsSe suggests an interpretation of the lowest energy interband transition in terms of an f+d excitation because of the strong and narrow line both in the diagonal and the off-diagonal conductivity. This assignment is corroborated by the absence of any sharp interband feature in the spectrum of ThAsSe.

A Lorentz-fit (eq. (19)) of the f+d peak in \( \sigma_{1xx} \) at room temperature reveals \( \hbar \omega_A = 0.74 \pm 0.02 \) eV, \( \hbar \gamma = 1.1 \) eV, \( f_{xx} = 2.35 \) and \( \langle \sigma_{xx} \rangle = 13 \times 10^{30} \) sec\(^{-2}\). The informations from \( \sigma_{xy} \) for the same transition at magnetic saturation are \( \hbar \omega_A = 0.74 \) eV and \( \langle \sigma_{xy} \rangle = 5.8 \times 10^{29} \) sec\(^{-2}\), which combines to \( \langle \sigma_{xy} \rangle / \langle \sigma_{xx} \rangle = 0.045 \). Neither in \( \sigma_{xx} \) nor in \( \sigma_{xy} \) any additional structure of the f+d transition is observed, which could point to a final state coupling of a localized f system. From these re-
sults the following conclusions about the $f$ density of states and spin-polarization may be drawn: i) The $f$ electrons form a narrow band at $E_F$, which is occupied by approximately three electrons. Correlation effects play a minor role, which is indicated by the absence of final state effects and by the large value of $f_{xx}$. ii) The $f$ spin-polarization is lower than in the uranium monochalcogenides and -pnictides, reaching a value of ~25% at magnetic saturation. This result is based on the assumption of atomic spin-orbit parameters (sec. 4.3.2.2) and the atomic model presented in sec. 3.2.2.

Consequently it may be stated, that the $f$ electrons are well described in a purely itinerant picture at least within the crystal planes perpendicular to the $c$-axis. This model is corroborated by the observation of a rather high $\gamma$-term in the electronic specific heat for UAsSe of $41mJ/mole*K^2$ [110]. For UAs, in comparison, the same size of $\gamma$ is observed ($\gamma = 53mJ/mole*K^2$ [48]) whereas it reaches only $0.5 mJ/mole*K^2$ [111] for ThAs.

In contrast to UAsSe, the low energy conductivity of ThAsSe is dominated by the conduction electrons (fig. 38). In the Drude theory of free carriers, which is expected to hold for $s$ and $d$ electrons of Th, the conductivity is given by:

$$\sigma_{1xx}(\omega) = \frac{\omega_p^2}{4\pi} \frac{\gamma^2}{\omega^2 + \gamma^2}$$

Therefore, from a plot of $1/\sigma_{1xx}$ versus $(\hbar\omega)^2$ one may obtain the size of $\omega_p^2$ and $\gamma$. In fact, fig. 40 visualizes Drude-behavior for ThAsSe in the energy range between 0.25 and 1.5 eV. The parameters of the linear fit in this figure are the uncoupled plasma frequency $\hbar\omega_p=7.15$ eV and $\hbar\gamma=1.0$ eV. From the definition $\omega_p^2=4\pi Ne^2/m^*$ and the assumption $m=m^*$, we compute a conduction electron concentration of $3.7\cdot10^{22}$ cm$^{-3}$, i.e. about 2.6 free electrons per formula unit for ThAsSe.

The number of charge carriers in UAsSe, on the other hand, is estimated to be less than 0.3 electrons per formula unit by a fit of $\sigma_{1xx}$ after subtraction of the $f+d$ contribution.

It becomes clear from these results, that the bonding is probable not identical in UAsSe and ThAsSe in spite of the similar lattice parameters, if the assumption $m=m^*$ holds for the conduction band in ThAsSe. While for the latter compound the charge transfer from cation to anion is only
1.3 electrons, 2.7 electrons of uranium contribute to bonding in UAsSe. These values are substantially lower than the 5 electrons, required to fill up the p bands of As and Se. Consequently, strong anion-anion bonding may be expected. Table 8 suggests, that mainly As-As and SeI-SeII bonds in the planes perpendicular to the c-axis may occur because these distances are only slightly larger than twice the atomic radii. This explanation works well for UAsSe, but it fails to account for the different bonding in ThAsSe, which has a larger unit cell than UAsSe. It is noteworthy to mention, that the number of d and s conduction electrons in UP₂, which exhibits a still larger unit cell, is found from transport measurements to be ≈2 electrons per formula unit [112].

6.2.2 The Valence Band

We have found in the last section, that the electronic density of states at \( E_F \) for UAsSe and ThAsSe is completely different. On the other hand, it is evident from figs. 37 and 38, that the optical spectra are quantitatively more similar at photon energies above ≈4 eV. In this latter energy range, the diagonal conductivity of the Th-compound is only a...
little more structured. This broad absorption band, centered at 6.9 eV, is assigned to the charge transfer transition of p valence electrons of As and Se into empty d states of Th or U. It is interesting to note, that no pronounced crystal field splitting is resolved in UAsSe although several peaks could be present for tetragonal crystal field symmetry, which is actually the case for ThAsSe (for tetragonal symmetry, both the t2g and the eg crystal-field level in cubic symmetry split into two subbands). This behavior of the two compounds may be caused by the different occupation of the d conduction band. Due to the larger number of overlapping p+d transitions in UAsSe, all structures may be smeared out.

The dominant structure at 4.3 eV in the off-diagonal conductivity of UAsSe (Fig. 39b) corresponds to the weak shoulder in $\sigma_{1xx}$ at the onset of valence band excitations. A very similar optical and magneto-optical response has been already discussed for UAs (sec. 4.2.2.3). Thus, it is obvious to assign this feature similar as for UAs to the excitation of bonding pd-electrons from the top of the valence band into spin-polarized f states, which explains the strong magneto-optical signal. The two valence band structures at 4.3 eV and 6.9 eV for UAsSe, therefore, reflect two different bonding states of anion p electrons with uranium d and s states, respectively.

6.3 Summary

In contrast to the expected localized behavior of the 5f electrons in UAsSe we found evidence for a f band at the Fermi energy, occupied by nearly three electrons. Despite the similar lattice parameters of ThAsSe compared to UAsSe, these two compounds show different cation-anion bonds most probably due to strong f-p hybridization. In Fig. 41, we have combined the findings from optical and magneto-optical spectroscopies in empirical energy level schemes for UAsSe and ThAsSe. In spite of the relatively high d density at $E_F$, the diamagnetism of ThAsSe can be explained by the diamagnetism of the inner shells, exceeding the Pauli-paramagnetism of the d states.

It should be noted, that the d band in UAsSe displays no exchange splitting as is evidenced by the same f+d transition energy in $\sigma_{xx}$ and $\sigma_{xy}$. This observation contrasts with the behavior of the uranium pnictides, where we have found exchange splittings in the order of 0.2 eV, although the f and d densities of states near $E_F$ seem to be similar in UAs and UAsSe.
Fig. 41: Empirical energy level schemes for UAsSe and ThAsSe as derived from optical and magneto-optical spectroscopies.

7. Th$_3$P$_6$-STRUCTURE COMPOUNDS

7.1 Introduction

U$_3$P$_6$ and U$_3$As$_6$ crystallize in the Th$_3$P$_6$-type bcc structure with four formula units per crystallographic unit cell. The two compounds order ferromagnetically at 138 and 198K with a saturation magnetization of 1.39 and 1.83\,$\mu_B$/U, respectively [113]. Unusually large magnetic [114, 115], magnetostrictive [116] and resistivity [117] anisotropy with respect to the (111)-direction, which is the easy axis of magnetization, have been reported. However, the magnetic moments on the uranium sites are not oriented along (111) but a noncollinear magnetic structure has been established [113]. Anisotropic pf-mixing has been introduced [118, 119] to explain the three axial structure with the observed tilting of the magnetic moment from the (111)-direction by about 20° within (110)-planes. The size of the pf-mixing energy for the two compounds was estimated to be
about 1eV [118,119]. And in fact, a careful analysis of optical data for Th₃P₄, Th₃As₄, U₃P₄, and U₃As₄ [120] strongly supports a mixing energy in this order of magnitude, which is assumed to be the driving force for the U-compounds to be metallic in contrast to the corresponding semiconducting Th-compounds. One conclusion from these optical data was, that the main effect of the pf-mixing is a shifting up of the p valence band by 0.85eV and pushing down the f states by the same amount of energy.

The optical conductivity σ₁xx was found to be dominated by strong excitations of the valence p electrons into the fourfold crystal field split d band superposed by a free carrier part at low energies. No f+d transitions could be identified. Consequently, the starting point of the magneto-optical investigation of these compounds was the question for the f binding energy. However, as we will see in the following, the observed magneto-optical spectra differ completely from the typical f+d response of all the materials discussed in the preceding chapters and it will be demonstrated that it is in fact not caused by f+d transitions.

7.2 Experimental Results and Discussion

The polar Kerr-effect of (112)-polished U₃P₄ and U₃As₄ crystals at magnetic saturation (B=4T, T=15K) is displayed in fig. 42. These spectra are

![Fig. 42: Polar Kerr-effect of (112)-polished U₃P₄ and U₃As₄ at magnetic saturation (B=4T, T=15K).](image-url)
characterized by an extremely large gradient of $\theta_K$ at low energies with a $\theta_K$ reaching absolute values of $6^\circ$ and a more or less flat behavior above $1.5eV$. Although these curves show some similarities with the Kerr-effect of the uranium monopnictides, the off-diagonal conductivity in fig. 43 clearly indicates a different behavior. The absorptive part of $\sigma_{xy}$ displays for both materials a general $\omega^{-1}$ decrease superposed by some weak structures. This general decrease strongly points to a dominant intraband contribution, although the possibility of an interband transition at an energy less than $0.5eV$ can not be excluded at this point of the analysis. However, if the magneto-optical feature would be caused by an interband transition, there should be a peak of at least $1.8 \times 10^{15}$ sec$^{-1}$ amplitude in $\sigma_{1xx}$ at the resonance energy, i.e. this transition would dominate $\sigma_{1xx}$ at $\hbar\omega < 1eV$ which is actually not observed [120]. Further, performing Kramers-Kronig transformations of $\sigma_{2xy}$ into $\sigma_{1xy}$ and vice versa (sec. 3.1) either with an extrapolation for an intra- or for an interband transition excludes the latter possibility and yields an extrapolation for $\hbar\omega < 0.5eV$ which is displayed in fig. 43. Hence we find a

![Graph showing off-diagonal conductivity of U_3P_4 and U_3As_4](image)

**Fig. 43:** Off-diagonal conductivity of U_3P_4 and U_3As_4 at magnetic saturation, calculated from the polar Kerr-effect and the optical data of ref. 120. The low energy extrapolation has been calculated by Kramers-Kronig inversion.
predominant free carrier contribution to the magneto-optical response in U₃P₄ and U₃As₄ in contrast to all other uranium compounds, discussed in the preceding chapters.

At zero energy, the extrapolation gives values for \( \sigma_{1xy}(0) \) in the order of \(-18 \times 10^{14} \text{ sec}^{-1}\). These numbers may be used as a further check of the extrapolation because they imply a positive Hall-resistivity of an extremal size. If the magneto-optical spectrum is governed by interband transitions, on the other hand, \( \sigma_{1xy}(0) \) would be expected to be much smaller because only free carriers contribute to \( \sigma_{1xy}(0) \). Using the relation between \( \sigma_{1xx}, \sigma_{1xy} \) and \( \rho_H \) (eq. (6)), we derive from our measurements a ratio \( \sigma_{1xy}(0)/\sigma_{1xx}(0) = \rho_H/\rho_0 \) of \(+1/1.8\) and \(+1/2.9\) for U₃As₄ and U₃P₄, respectively. These results are in favorable agreement with transport measurements [121] giving \(+1/2.3\) and \(+1/2.8\) for the two compounds with absolute values of \( \rho_H \) in the order of \(200 \mu\Omega \text{cm} \) at \( T<<T_c \).

Thus, this comparison with transport data evidences that the magneto-optical spectrum is in fact determined by the \( \omega^{-1} \) dependent term in \( \sigma_{xy} \) (eq. (9)) and the important result of a negative charge carrier spin-polarization emerges from the sign of \( \sigma_{xy} \).

Of course the question now arises, what are the microscopic origins of this large intraband effect in particular if it is noticed, that for other ferromagnetic materials like the uranium chalcogenides, the ratio \( \rho_H/\rho_0 \) is at least one order of magnitude smaller [72]. To derive the parameters of eq. (9), we have performed a fit of the line-shape and the size of \( \sigma_{xy} \), taking the ratio \( \omega_p^2/4\pi \gamma \) from \( \sigma_{1xx}(0) \). The spin-orbit term (eq. (10)) has been assumed to be the same as in the UX compounds, i.e. we take \( 1 \text{ eV} \) for both \( \hbar \omega_{\text{so}} \) and \( \hbar \omega_{\text{so}} \). The main results of this fit are:

i) the charge carriers are totally spin-polarized and their moment is antiparallel to the f-moment, i.e. \( \sigma_d = -100\% \);

ii) the unscreened plasma frequencies are \( 4 \) and \( 4.7 \text{ eV} \) for U₃As₄ and U₃P₄, respectively, which yields a number of \( 0.6 \) and \( 0.75 \) charge carriers per uranium within the assumption \( m=m^* \). These values are by far larger than the carrier densities derived from de-Haas-van-Alphen measurements [122] and point to undetected orbits in those experiments as the authors did intimate.

The weak structures in \( \sigma_{2xy} \) of both compounds (fig. 43) indicate, that apart from the prevailing intraband part, magneto-optical signals from interband transitions are present. To suppress the \( \omega^{-1} \) dependence, it is convenient to discuss \( \omega \sigma_{2xy} \), which is displayed in fig. 44 for U₃P₄.
Fig. 44: Experimental values of $\omega \sigma_{2xy}$ for $U_3P_4$ at magnetic saturation. The area under the solid line is the estimated intraband contribution, derived from a fit of $\sigma_{xy}$. At the top of this figure, the absorptive diagonal conductivity from ref. 120 is displayed for comparison.

The solid line in this figure shows the free carrier contribution as derived from the fit of $\sigma_{xy}$, which becomes energy independent in $\omega \sigma_{2xy}$ for $\Gamma_{20}$[120]. For comparison with normal optics, we have added in this figure the absorptive diagonal conductivity $\sigma_{1xx}$ [120]. It becomes clear, that each peak in $\sigma_{1xx}$ corresponds to a structure in $\omega \sigma_{2xy}$, i.e. no unresolved transitions in $\sigma_{1xx}$ can be identified by magneto-optics.

The detailed analysis of $\sigma_{1xx}$ for U and Th tetranictrides has revealed an assignment of the four lowest energy structures in fig. 44 to p excitations into the crystal field split d band. In the context of this investigation, the structures observed in $\omega \sigma_{2xy}$ correspond to the same transitions. This picture is supported by the relatively small total weights $\langle \sigma_{xy} \rangle$ for a ferromagnetic 5f material, reaching $=2.5\times10^{29}$ sec$^{-2}$ for the lowest energy peak and $=6\times10^{28}$ sec$^{-2}$ for each of the other struc-
tures. The peak at 5eV, however, which has been tentatively assigned to a \( f+d \) transition, seems also to be due to a \( p \) excitation, because the magneto-optical signal is as weak as for the other transitions and because there is no reason from selection rules, that \( f \) excitations into the lower lying \( d \) crystal field levels should not occur.

Hence we are left with the situation, that no \( f+d \) transitions are observed in the magneto-optical spectra and therefore the nature of the \( f \) states in \( \text{Th}_3\text{P}_4 \)-structure compounds is still a subject of speculations. However, it can not be excluded, that the \( f+d \) transitions are energetically degenerated with the \( p+d \) transitions, i.e. the huge peaks in \( \sigma_{1xx} \) display mainly \( p \)-excitations whereas the sharp structures in \( \omega\sigma_{2xy} \) correspond merely to \( f+d \) transitions at the same energy.

8. SOME ASPECTS OF THE TECHNICAL APPLICATION OF MAGNETO-OPTICS

To realize the importance of magnetic storage technologies in the today's industrial market one has to notice that the fabrication of magnetic storage products already exceeds the semiconductor output.

For longitudinal recording (i.e. in plane magnetization like tapes, hard-discs, floppy-discs etc.) the physical limits of bit-density and access-time seem to be reached [123]. In particular, serious mechanical difficulties arose. For example, the flying height of the recording head had to be reduced down to less than 0.2\( \mu \)m to achieve the highest bit densities of a few Mbit/cm\(^2\) in longitudinal recording. Parallel to the reduction of the gap between recording head and material, the size of the recording head itself was miniaturized down to a few \( \mu \)m side length.

To achieve an additional progress in storage density, vertical recording (i.e. magnetization perpendicular to the surface of the storage material) is intensively studied today on a research level. With this type of recording, the bit density may be further increased by a factor of three. However, the important mechanical difficulties remain and new trouble comes up e.g. due to the stray field of the recording head [123]. To avoid these problems, several techniques of optical recording have been developed in the last decade. They allow bit densities of several \( 10^7 \) bit/cm\(^2\), determined by the wavelength of the used laser. One of the very few erasable techniques takes advantage of the polar magneto-optical effects, i.e. the Faraday-effect in transmission or the polar Kerr-effect in re-
Fig. 45: Viewing of magnetic domains using the polar Kerr-effect and polarization optics.

reflection. Fig. 45 shows a typical setup for the latter configuration. The linear polarization of the incident light which is reflected from domains with magnetization parallel or antiparallel to the direction of light propagation is rotated by $\theta_K$ and $-\theta_K$, respectively. Hence, using an analyser perpendicular to the one polarization, the figure of merit $n$ for the read-out process is defined by

$$n = R \sin^2 2\theta_K$$

(29)

where $R$ is the reflectivity of the storage material. A similar equation holds for the Faraday configuration, but with $R$ replaced by the transmitted light intensity $e^{-Kd}$ (where $K$ is the absorption constant and $d$ is the thickness of the storage material) and of course $\theta_K$ replaced by the Faraday-rotation $\theta_F$. To achieve a high $n$ and hence to render possible a high data rate, large magneto-optical effects are required.

But first let us discuss which of the two polar magneto-optical effects dominates for a given material with optical indices $n$ and $k$ and with a magneto-optical activity $\sigma_{xy}$. The complex polar Kerr-effect is determined by [124]
\[ \phi_K = \Theta_K + i\epsilon_K = -i\epsilon_{xy}/\sqrt{\epsilon_{xx}}(\epsilon_{xx}-1) \]  

(30)

where \( \sigma_{ij} \) and the dielectric tensor \( \epsilon_{ij} \) are connected by \( \epsilon_{ij} = \delta_{ij} - i4\pi\sigma_{ij}/\omega \) with the Kronecker-Delta \( \delta_{ij} \). Using the same optical functions, the complex Faraday rotation is given by [124]

\[ \phi_F = \Theta_F + i\epsilon_F = -(\pi d/\lambda)\epsilon_{xy}/\sqrt{\epsilon_{xx}} \]  

(31)

The combination of these equations results in

\[ \frac{\phi_F}{\phi_K} = \frac{\pi d}{\lambda} \left| (\epsilon_{xx} - 1) \right| = \frac{2\pi d}{c} \left| \sigma_{xx} \right| \]  

(32)

This interesting result postulates, that the relative size of Faraday and Kerr-effect simply is proportional to the diagonal conductivity \( \left| \sigma_{xx} \right| = \left| \sigma_{1xx} + i\sigma_{2xx} \right| \). Taking for the Faraday configuration a transmittance of 37% (i.e. \( d=1/K \)), which is in the order of typical reflectivities, eq. (32) has been computed as a function of \( n \) and \( k \) and is displayed in fig. 46. The quite surprising result is, that the Faraday effect exceeds the

Fig. 46: Ratio of the total Faraday and Kerr-signals for a material with optical constants \( n \) and \( k \). The area of fundamental absorption in the \( n-k \) plane is indicated for: a) \( f+d \) transition in Eu-chalcogenides [66]; b) \( f+d \) transition in U-chalcogenides; c) \( d \) excitations in Fe, Co, Ni [125, 126]; d) plasma-edge splitting [30].
Kerr-effect for nearly all physical combinations of $n$ and $k$. In particular, in the case of typical magneto-optical active interband transitions in 3d, 4f and 5f materials, the ratio $|\phi_F/\phi_K|$ is about 2. However, taking photon energies in the gap of magnetic semiconductors, this ratio may be orders of magnitude larger (e.g. YIG). The only known magneto-optical effect which results in a dominant Kerr-rotation is the plasma-edge splitting of the conduction electrons [30].

For these reasons, mainly transparent thin films are used for storage applications. If a reflection configuration is required by reasons of the design (e.g. erasable compact disc), double Faraday-rotation rather than single Kerr-rotation is applied [123].

To elucidate the strength of the magneto-optical activity in the fundamental absorption regime of the known magnetic materials, let us compare the polar Kerr-rotation. In the group of 3d and 4f metals and metallic compounds, the typical rotation is $0.\varphi$ or less [27, 125-128]. Exceptions are some compounds with extraordinary electronic structure (e.g. half-metallic ferromagnets), where $\Theta_K$ may reach $1.2\varphi$ [129]. The largest rotations up to now have been reported for magnetic semiconductors with $\Theta_K$ up to $\varphi$, which have, however, very low Curie-temperatures [130-132]. In the present work, on the other hand, new materials with ordering temperatures up to 210K have been reported, showing single Kerr-rotations up to $\varphi$ at 65% reflectivity. In addition it has been shown that the maximum Kerr-rotation may be adjusted to a given photon energy by varying the composition of the compounds. Fig. 47 displays in example the Kerr-rotation in (100)-direction of the system $USb_xTe_{1-x}$ for different $x$ (in (111)-direction, the rotation is larger by a factor of 1.45 (fig. 27)). The peak position shifts between 1.7 and 0.5eV with Te-concentration.

In fig. 48, we have collected the largest values of the 'figure of merit' $\eta$ versus energy for the investigated 5f materials. For comparison, $\eta$-values of some 3d and 4f compounds which have been considered for application are included. This collection shows, that the 'figure of merit' of the present uranium compounds exceeds those of all other materials known up to now by at least one order of magnitude. The only restriction for a successful application in storage devices may be, that the Curie Temperatures of about 200K are below room temperature. In future, this shortcoming may perhaps be overcome by an appropriate alloying although the magnetic moment on the uranium sites in the known systems with $Tc>300K$ decreases to very low values. However, a specific search for such systems has not yet been done.
Fig. 47: Polar Kerr-rotation of four different (100)-oriented cleaved USb\(_x\)Te\(_{1-x}\) single crystals at magnetic saturation. For clarity, the curves with \(x=0.8, 0.5\) and 0 are vertically shifted by 2, 4 and 7 degrees, respectively.

Fig. 48: Read-Out efficiency \(R \sin^2 2\theta_K\) versus photon energy of some uranium compounds at magnetic saturation. For comparison, we have added the values for CoCr\(_2\)S\(_4\) [130], MnBi [133], PtMnSb [129] and Y\(_2\)BiFe\(_2\)O\(_{12}\) [134].
It has been demonstrated during this work, that the investigated metallic uranium compounds may be classified in two groups of distinct magneto-optical response of the 5f electrons.

The materials of the first class including uranium-monochalcogenides, monopnictides and pseudo-binaries between the chalcogenides and pnictides but also diluted uranium in a nonmagnetic NaCl-structure matrix and certain ternary compounds display a strong magneto-optical response proportional to the density of uranium ions and to the magnetic moment per uranium. The ground state for these compounds has been evidenced to be a narrow f band occupied by nearly three electrons. The 'diamagnetic' line shaped signal of the f-d transition in $\sigma_{xy}$ is well understood in size and shape by a band model.

For the second class of the investigated magnetic uranium compounds like those with a Th$_3$P$_4$ crystal structure or certain intermetallics like Ulr, the magneto-optical signal from interband transitions was found to be too small for an unambiguous identification of f-excitations. However it may be stated, that the Kerr-response of the 5f electrons is reduced by at least a factor of 50 compared to the first group of materials, if it is present at all. Concerning the reasons of this unexpected behavior we can only speculate. The magneto-optical signal may be reduced either by a small radial overlap integral for localized states or by a singlet crystal field ground state or by the fact, that the moment on the uranium sites contributes only little to the total moment as it is well known for UFe$_2$. A further study of uranium intermetallics seems to be a promising field for new and fascinating results.

For uranium systems with almost trivalent uranium, the off-diagonal conductivity reaches values up to $\sigma_{xy}/\sigma_{xx}$=0.35, which approaches the theoretical limit of 2/3 and is considerably larger than in 3d and 4f metals with a ratio of typically $10^{-3}$. May it may be stated, that the observed magneto-optical effects nearly reach the largest possible values in principle. The reason is, that on the one hand, $\sigma_{xy}$ is proportional to the total magnetic moment, which becomes larger for more localized states, but on the other hand, $\sigma_{xy}$ also is proportional to the radial overlap integral, which is known to decrease strongly with localization. Hence the investigated compounds display an almost optimal degree of itinerancy regarding extremal Kerr-signals.
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    Austauschinduzierte Plasmakantenaufspaltung der Tm-Chalcogenide

12. W. Reim, J. Schoenes
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Magnetische Rotverschiebung des f-d Übergangs in USB₀.₉Te₀.₁ 

First Magneto-Optical Observation of an Exchange Induced Plasma Edge Splitting 

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Magneto-Optical Investigation of the Electronic and Magnetic Structure of UAsₓSe₁₋ₓ 

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Magneto-Optics of Semiconducting, Intermediate Valant and Metallic Tm-Chalcogenides 

Optics and Magneto-Optics of UAsSe 
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ORAL PRESENTATIONS

1. Evidenz für jj-Kopplung beim f + d Uebergang in UO₂
   Spring meeting of the German Physical Society, Münster,
   West Germany
   10.3.1981

2. Characteristics of Magneto-Optical Spectra and 3d-Localized
   States in Pure and Substituted Magnetite
   Fall meeting of the Swiss Physical Society, Davos, Switzerland
   24.9.1981

3. Magneto-Optische Untersuchungen der elektronischen Struktur
   von reinem und substituiertem Magnetit
   Tagung über "Optische Eigenschaften magnetisch geordneter
   Materialien", Bad Honnef, Germany
   21.10.1981

   Spring meeting of the German Physical Society, Münster,
   West Germany
   1.4.1982

5. Kerr-effect and Dielectric Tensor Elements of Magnetite and
   other Transition Metal Compounds: Evidence of Final State
   Coupling
   EUCHEM Conference on Magnetic Circular Dichroism and Rela¬
   ted Magneto-Optical Techniques, Leuven, Belgium
   29.9.1982

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   7.10.1982

7. Neue Kerr-Rotatoren mit der grössten 'figure of merit'
   Spring meeting of the Swiss Physical Society, Fribourg,
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   24.3.1983

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   3rd General Conference of the Condensed Matter Division of
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9. Magnetische Rotverschiebung des f+d Uebergangs in
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   zerland
   14.10.1983
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   4.11.1983

11. Magneto-Optics and Electronic Structure of Uranium-monochalcogenides
    29th Conference on Magnetism and Magnetic Materials, Pittsburgh, Pennsylvania, USA
    9.11.1983

12. First Magneto-Optical Observation of an Exchange Induced Plasma Edge Splitting
    29th Conference on Magnetism and Magnetic Materials, Pittsburgh, Pennsylvania, USA
    9.11.1983

13. Magnetic Exchange and Spin-Polarization in Uranium-Monopnictides
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    Seminar at IBM Rüschlikon, Rüschlikon, Switzerland
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17. Der polare Kerr-Effekt von Uranverbindungen
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    29.11.1984

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- Magneto-optics at low temperatures (2K) and high magnetic fields (10T).
- Different methods of optical measurements.
- UHV technique.
- Thin film preparation by different methods.
- Atomic models including crystal-field, spin-orbit and final state coupling effects for different systems like Fe₃O₄, TmSe₀.₆₅Te₀.₃₅ and UO₂.
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