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Relativistic calculations of the magneto-optical Kerr spectra in (001) and (111) US, USe, and UTe

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The magneto-optical (MO) Kerr spectra of the isochemical uranium compounds US, USe, and UTe are investigated from first principles, using density-functional theory in the local spin-density approximation and the relativistic augmented-spherical-wave band-structure method. Fully relativistic, optical transition-matrix elements are derived from Dirac theory. The *ab initio* calculated Kerr spectra compare reasonably well with experimental spectra in height, but the theoretical spectra exhibit a double peak structure, whereas the experimental ones show only one peak and a vague shoulder. To explain this difference, attention is first given to anisotropy effects related to the strong magnetic anisotropy present in these compounds. Polar Kerr spectra are calculated for two magnetization directions, the (001) and (111) (i.e., easy axis) directions. A clear anisotropy is found in the Kerr spectra of these two magnetizations, but the differences between experimental and theoretical spectra cannot be related to the magnetic anisotropy. Secondly, the influences of the lattice spacing and of an external magnetic field on the Kerr spectra are investigated, but no explanation of the differences found can be derived thereof. The band structures and Kerr spectra obtained by the ASW method are furthermore checked by recalculating them with a fully relativistic linear muffin-tin orbital scheme and are found to be essentially the same. The positions of the *ab initio* energy bands are in addition in accordance with experimentally determined band positions. The origin of the difference in the Kerr spectra is discussed in relationship to electron-correlation effects and to the orbital polarization.

I. INTRODUCTION

The uranium compounds US, USe, and UTe belong to the class of uranium monochalcogenides that crystallize in the NaCl structure and order ferromagnetically (on the uranium sublattice) at Curie temperatures of 178, 160, and 102 K, respectively (see, e.g., Ref. 1). These uranium compounds exhibit several unusual physical phenomena, which are the reason for an as-yet ongoing interest in these compounds. Despite their relatively simple and highly symmetrical NaCl structure, it has been found that the magnetic ordering on the uranium atoms is strongly anisotropic,[2,3] with the uranium moment favoring a (111) alignment. The magnetic anisotropy in US, e.g., is one of the largest measured in a cubic material, with a magnetic anisotropy constant K_1 of more than 2×10^8 erg/cm^3.[4] Also the magnetic moment in itself is unusual, consisting of an orbital moment that is about twice as large as the spin moment and of opposite sign,[5–7] but it is not close to the atomic moment. In addition to this, these materials show with increasing mass of the chalcogenide atom evidence of correlated-electron behavior, with UTe being considered as a dense Kondo system.[8] Obviously, the uranium $5f$ electrons are to be held responsible for both features.

Schoenes and Reim[9–12] investigated the magneto-optical (MO) spectra of these uranium salts and obtained three rather similar Kerr spectra, as one would expect from isochemical compounds. Yet, the measured Kerr rotation spectra are unusually large, with peak values of about 3°. In an interpretation of their measurements Reim and Schoenes gave an analysis of the Kerr spectra in terms of optical transitions on uranium.[10,11] More recently, several theoretical investigations of the MO spectra employing *ab initio* band-structure calculations have been undertaken. The optical conductivity spectra of US have been calculated by Haliliov and Kulatov,[13] Gasche,[14] and Brooks, Gasche, and Johansson,[15] whereas Cooper and co-workers computed the optical conductivity spectra of US and UTe.[16,17] So far the Kerr spectra of US were only calculated by Gasche[14] and Brooks, Gasche, and Johansson,[15] and by Osterloh *et al.*[18] These theoretical spectra are all computed from first principles, using Kubo linear-response theory,[19] but it appears that there are large differences among them. Cooper and co-workers[16,17] find good agreement with experiment for the real part of the diagonal conductivity ($\sigma_{xx}^{(1)}$) of UTe,[16] but the much more complicated off-diagonal conductivity ($\sigma_{xy}^{(2)}$) of US and UTe is about 4 times larger than experiment and also the shape of their spectrum is different from the experimental one. Halilov and Kulatov[13] also find an off-diagonal conductivity which is much larger than the experimental one, but they additionally obtain a diagonal conductivity $\sigma_{xx}^{(1)}$ that differs substantially from experiment. Gasche and Brooks[14,15] find a Kerr rotation spectrum that is quite different from experiment, and subsequently consider the effects of an orbital-polarization term to improve the *ab initio* Kerr spectra. Osterloh *et al.*[18] obtained for US reasonable agreement with experiment for the absolute value of the Kerr spectra and partial agreement for the shape of the Kerr spectra. The latter investigation can be considered as a preliminary study of the present work, since in part the same computational method was used.[20] In view of the similar band-structure methods that are being used, it can be anticipated that the differences that are present in the various first-principles magneto-optical spectra are likely related to the computational difficulties that must be mastered in computing such spectra.[20] Although undoubtedly strong electron correlations exist within the uranium $5f$ electrons, it is, in our opinion, too early to attribute any deviation found between experimental and theoretical MO spectra to a failure of the local spin-density approximation (LSDA) used in the underlying band-structure calculation. In an attempt to find out what can be described within the LSDA band picture and what is outside of its scope, we first compare the MO spectra with experiment, and then try to analyze the origin of the differences found.

In the present paper we investigate therefore in detail the MO spectra of the uranium chalcogenides. First, we derive fully relativistic, optical transition-matrix elements. These transition-matrix elements contain thereby relativistic corrections that were ignored in all earlier calculations. Second, we study the polar Kerr spectra for two magnetization orientations, the (001) and (111) orientations. The measurements of Reim and Schoenes[11,12] were made along the (001) axis, but the easy axis in these compounds is the (111) axis.[3,4] Therefore these measurements can, strictly speaking, not be called polar Kerr measurements. By comparing the theoretical polar Kerr spectra of the (001) and (111) magnetizations an estimation of the anisotropy contribution to the Kerr spectra can be made. Third, we investigate the influence of the lattice spacing on the theoretical Kerr spectra. This is of relevance, as small changes in the lattice spacing might affect the position of the uranium $5f$ bands. Fourth, in order not to rely on the particular computational method used, we have verified our results by recalculating them with an independent computational scheme, and have found that the thus obtained *ab initio* MO spectra are in excellent agreement. Furthermore, we also compare the LSDA band structures with experimentally determined band positions, and the calculated moments with the experimental ones. The effect of a different uranium spin and orbital moment is studied by computing the Kerr spectra in an applied magnetic field. Last, we discuss the possible effects of electron correlations and of an orbital polarization on the Kerr spectra.

II. RELATIVISTIC MATRIX ELEMENTS

The approach used in the present work for describing the magneto-optical spectra is the conventional band-structure approach. In this approach, the optical spectra result from optical transitions taking place between occupied and unoccupied band states. The energy-band description has been found to be fully satisfactory for the Kerr spectra of transition metals and transition-metal compounds.[20–23] The Kerr spectra are directly obtainable from the optical conductivity tensor $\boldsymbol{\sigma}$, through

$$\Phi_K(\omega) = \theta_K(\omega) + i\varepsilon_K(\omega) = \frac{-\sigma_{xy}(\omega)}{\sigma_{xx}(\omega)\left(1 + \frac{4\pi i}{\omega}\sigma_{xx}(\omega)\right)^{1/2}} . \tag{1}$$

The optical conductivity $\boldsymbol{\sigma}$ can be evaluated using the Kubo linear-response expression.[19] When empirical lifetime effects are taken into account, the expression for the conductivity tensor is given by (see Ref. 24)

$$\sigma_{xy}(\omega) = \frac{ie^2}{m^2\hbar V_{\rm uc}} \sum_{\mathbf{k}} \sum_{\ell\,{\rm occ}} \sum_{n\,{\rm un}} \frac{1}{\omega_{nl}(\mathbf{k})} \left(\frac{\Pi^x_{ln}\Pi^y_{nl}}{\omega - \omega_{nl}(\mathbf{k}) + i\delta} + \frac{(\Pi^x_{ln}\Pi^y_{nl})^*}{\omega + \omega_{nl}(\mathbf{k}) + i\delta} \right) , \tag{2}$$

$$\sigma_{xx}(\omega) = \frac{ie^2}{m^2\hbar V_{\rm uc}} \sum_{\mathbf{k}} \sum_{\ell\,{\rm occ}} \sum_{n\,{\rm un}} \frac{1}{\omega_{nl}(\mathbf{k})} \left(\frac{|\Pi^x_{ln}|^2}{\omega - \omega_{nl}(\mathbf{k}) + i\delta} + \frac{|\Pi^x_{ln}|^2}{\omega + \omega_{nl}(\mathbf{k}) + i\delta} \right) , \tag{3}$$

with $\hbar\omega_{nl} = E_n(\mathbf{k}) - E_l(\mathbf{k})$ the energy difference of the bands where the optical transition takes place and $V_{\rm uc}$ the unit-cell volume. The phenomenological lifetime relaxation is included through $\delta = 1/\tau$, τ being the relaxation time. The $\mathbf{\Pi}_{nl}$ originate from $[H, \mathbf{r}]$, H being the Kohn-Sham Hamiltonian, and are usually computed as

$$\mathbf{\Pi}_{nl}(\mathbf{k}) = \int \psi_{n\mathbf{k}}(\mathbf{r})\, \mathbf{p}\, \psi_{\ell\mathbf{k}}(\mathbf{r}) d\mathbf{r} , \tag{4}$$

with $\mathbf{p} = -i\hbar\boldsymbol{\nabla}$, and $\psi_{n\mathbf{k}}$ the Bloch electron-wave function. Although this form of the momentum operator (containing the canonical momentum $\mathbf{p}$) is generally used, it is, strictly speaking, only valid in the nonrelativistic limit. The Kerr effect, however, is known to be purely relativistic in origin.[25] Yet, even if the nonrelativistic expression (4) for $\mathbf{\Pi}$ is used, relativistic effects enter in the matrix elements through the electron-wave functions in Eq. (4). In itself it is quite simple to give a fully relativistic expression for the matrix elements when one computes the energy-band structure using the (four component) Dirac equation. In this case, the momentum operator is directly given by the matrix elements of $mc\boldsymbol{\alpha}$ (standard Dirac notation) (see, e.g., Refs. 26,27). But when one calculates the band structure using the scalar-relativistic Schrödinger equation with spin-orbit (SO) coupling included through a second variation, as we do in the present work, an appropriate relativistic expression for the matrix elements must be rederived. Already Wang and Callaway[24] gave a partial relativistic extension by including a spin-orbit part, namely, $\mathbf{p} + (\hbar/4mc^2)[\boldsymbol{\sigma} \times \boldsymbol{\nabla} V(\mathbf{r})]$. In this form, the momentum operator corresponds to the nonrelativistic Schrödinger equation plus an additional SO term. In the following an appropriate expression is derived.

To this end, we start from the Dirac equation in standard notation,

$$\left[c\boldsymbol{\alpha}\cdot\mathbf{p} + \beta mc^2 + V + V_{\mathrm{sp}}\beta\sigma_z\right]\psi = E\psi\,, \tag{5}$$

with V_{sp} the spin-polarized part of the exchange-correlation potential along the quantization z axis (see, e.g., Refs. 26,28–32, and references therein for current approaches to relativistic energy-band theory). All other parts of the potential are contained in V. The four-vector ψ can be expressed in the large and small spinor components, through $\psi = \binom{\psi^u}{\psi^\ell}$. Eliminating the small component ψ^ℓ from Eq. (5) gives the Hamiltonian equation for the large component,

$$H^u\psi^u = E^u\psi^u\,, \tag{6}$$

with

$$H^u = c^2\left[\mathbf{p}\cdot(Q_1 + Q_2\sigma_z)\mathbf{p} + i\boldsymbol{\sigma}\cdot\mathbf{p}Q_1\times\mathbf{p} + i\mathbf{e}_z\cdot\mathbf{p}Q_2\times\mathbf{p} - p_zQ_2\boldsymbol{\sigma}\cdot\mathbf{p} - \boldsymbol{\sigma}\cdot\mathbf{p}Q_2p_z\right] + V + V_{\mathrm{sp}}\sigma_z \tag{7}$$

and

$$E^u = E - mc^2\;,\quad Q_1 = \frac{E^u + 2mc^2 - V}{(E^u + 2mc^2 - V)^2 - V_{\mathrm{sp}}^2}\;,\quad Q_2 = \frac{V_{\mathrm{sp}}}{(E^u + 2mc^2 - V)^2 - V_{\mathrm{sp}}^2}\,. \tag{8}$$

This expression can be rewritten further, but we omit details here. For the corresponding momentum operator we use the definition

$$\boldsymbol{\Pi} = \frac{im}{\hbar}\left[H^u, \mathbf{r}\right]. \tag{9}$$

This leads to the following expression for $\boldsymbol{\Pi}$:

$$\frac{1}{mc^2}\boldsymbol{\Pi} = (Q_1 + Q_2\sigma_z)\mathbf{p} + \mathbf{p}(Q_1 + Q_2\sigma_z) + i\boldsymbol{\sigma}\times(\mathbf{p}Q_1) + i\mathbf{e}_z\times(\mathbf{p}Q_2) - \boldsymbol{\sigma}[Q_2p_z + p_zQ_2] - \mathbf{e}_z[Q_2\boldsymbol{\sigma}\cdot\mathbf{p} + \boldsymbol{\sigma}\cdot\mathbf{p}Q_2]\,. \tag{10}$$

In this form, $\boldsymbol{\Pi}$ is exact in all orders of $1/c$ and valid for the scalar-relativistic Hamiltonian plus spin-orbit interaction. Standard operator notation has been used here, except when the canonical momentum $\mathbf{p}$ and a scalar function are enclosed in round brackets, then the operator is supposed to act on this function only. The function $Q_1 + Q_2\sigma_z$ in (10) can be interpreted as a relativistic, energy-, and spin-dependent inverse mass.

To understand better the meaning of the individual terms in Eq. (10), it is elucidating to consider an expansion of (10) in lowest order of $1/c^2$. This gives the following expression for $\boldsymbol{\Pi}$:

$$\begin{aligned}\boldsymbol{\Pi} \approx \mathbf{p} + \frac{1}{4mc^2}\Big\{&(-E^u + V + V_{\mathrm{sp}}\sigma_z)\mathbf{p} + \mathbf{p}(-E^u + V + V_{\mathrm{sp}}\sigma_z) + i\boldsymbol{\sigma}\times(\mathbf{p}V)\\ &+ i\mathbf{e}_z\times(\mathbf{p}V_{\mathrm{sp}}) - \boldsymbol{\sigma}[V_{\mathrm{sp}}p_z + p_zV_{\mathrm{sp}}] - \mathbf{e}_z[V_{\mathrm{sp}}\boldsymbol{\sigma}\cdot\mathbf{p} + \boldsymbol{\sigma}\cdot\mathbf{p}V_{\mathrm{sp}}]\Big\}\,.\end{aligned} \tag{11}$$

The dependence of this expression on the specific energy of the state considered can furthermore be removed, using the approximation $E^u - V - V_{\mathrm{sp}}\sigma_z \approx p^2/2m + \mathcal{O}(1/c^2)$, which leads to

$$\boldsymbol{\Pi} \approx \mathbf{p} + \frac{1}{4mc^2}\left(-\frac{p^2}{m}\mathbf{p} + (\mathbf{p}[V + V_{\mathrm{sp}}\sigma_z]) + i\boldsymbol{\sigma}\times(\mathbf{p}V) + i\mathbf{e}_z\times(\mathbf{p}V_{\mathrm{sp}}) - \boldsymbol{\sigma}[V_{\mathrm{sp}}p_z + p_zV_{\mathrm{sp}}] - \mathbf{e}_z[V_{\mathrm{sp}}\boldsymbol{\sigma}\cdot\mathbf{p} + \boldsymbol{\sigma}\cdot\mathbf{p}V_{\mathrm{sp}}]\right). \tag{12}$$

From this expansion one can now recognize that the second term on the right-hand side of (12) is related to the so-called mass-velocity term, and that the third term relates to the Darwin correction. The fourth term contains the spin-orbit interaction, which was in this form already derived by Wang and Callaway.[24] The other terms have no special names, but they are of the same order of $1/c^2$. They are related to the coupling of the exchange-correlation (or magnetic) field (here taken parallel to the z axis) to the spins of the electrons. With respect to the electron spin, we remark that the fourth, sixth, and seventh term in Eqs. (10)–(12) can cause spin-flip optical transitions.

In the present work, we have decided to use expression (10) to evaluate $\boldsymbol{\Pi}$, but with the additional approximation that the dependence on the energy E^u has been neglected. This can be done, because in the present calculations only valence states near the Fermi energy are considered, whereas the relativistic corrections become noticeable only close to the nucleus. But, in despite of this fully relativistic formulation, we have found so far that for optical transitions between valence states the effect of the relativistic corrections on the Kerr spectra is not more than two percent, even for uranium compounds. Their effects might, however, be larger when deep-lying core states are involved in the transition.

Previously it has been shown for the momentum operator in the form of the canonical momentum **p** [Eq. (4)], that it is important to evaluate its matrix elements by including so-called combined corrections in the integral (4), which improve the convergence of the angular momentum sums occurring in the expression for **Π** (see Ref. 20). This approach leads to matrix elements that are much more accurate. In the present formulation the matrix elements, though of different form, must also be evaluated using combined corrections. This has been programmed in the numerical evaluation of the integral, but we omit to outline this technical detail here. To end with, we mention that the present evaluation of the matrix elements is restricted by the spherical potential approximation, which is imposed by the band-structure method used. An evaluation of the matrix elements within a full-potential band-structure calculation might improve the accuracy of the matrix elements. So far, however, we have found that the matrix elements in the spherical approximation give a rather satisfactory description of the MO spectra of transition-metal compounds.[20,23]

III. RESULTS FOR US, USe, AND UTe

With the above given formalism, the theoretical Kerr spectra of the uranium chalcogenides have been calculated in the polar geometry (i.e., incident light beam and magnetization perpendicular to the surface), for two orientations of the uranium moment, the (001) and (111) directions. These two directions have been chosen in order to compare to the experimental Kerr spectra.[10–12] The measurements of the Kerr spectra of these compounds were performed in the geometry where the surface is perpendicular to the (001) direction, but with the magnetic moment in the (111) direction. Neither of the calculated orientations corresponds to this geometry, but at least the importance of the orientation on the Kerr spectra can be estimated in this way. The band-structure calculations have been performed with the augmented-spherical-wave (ASW) method,[33,34] which is an energy-linearized band-structure approach similar to the linear muffin-tin orbital (LMTO) method.[35] In all calculations, *spd* augmented waves have been used on the chalcogenide atom, and *spdf* states on uranium. For the LSDA exchange-correlation potential the von Barth–Hedin parametrization[36] has been exploited. Experimental lattice constants[12] have been used.

To start with, we show the theoretical Kerr rotation and Kerr ellipticity spectra of the uranium monochalcogenides together with experimental spectra in Figs. 1 and 2, respectively. All theoretical Kerr spectra presented in Figs. 1, 2 have been calculated with an inverse lifetime parameter of 0.4 eV, and without a phenomenological intraband conductivity added. Several observations can be made from the spectra shown in Figs. 1 and 2. In the first place, it can be concluded that the heights of the Kerr rotation and of the Kerr ellipticity spectra are properly given by theory. However, the shape of the rotation spectra in the energy region of the main peak (1–3 eV) is not reproduced by theory, since the theoretical spectra exhibit a double-peak structure. Also in the theoretical ellipticity spectra this double-peak structure is reflected. Above 3 eV the experimental and theoretical Kerr rotation spectra are of the same shape, though be it that the zero-crossing energy is shifted by 1–1.5 eV to a higher energy as compared to experiment. In general, both the experimental Kerr rotation and ellipticity spectra are narrower than their theoretical counterparts. We note further that there is only a small dependence of the theoretical Kerr spectra on the magnetization orientation. Thus, the calculated anisotropy is small enough to warrant already the conclusion that the difference be-

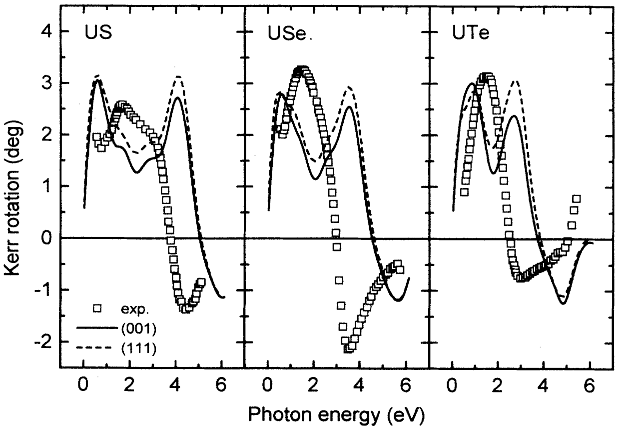

FIG. 1. Calculated polar Kerr rotation spectra of the uranium monochalcogenides US, USe, and UTe, for the (001) and (111) orientations of the magnetic moment. The theoretical spectra given result from interband optical transitions only, and are calculated with a relaxation-time broadening of 0.4 eV. The experimental data given are those of Ref. 10.

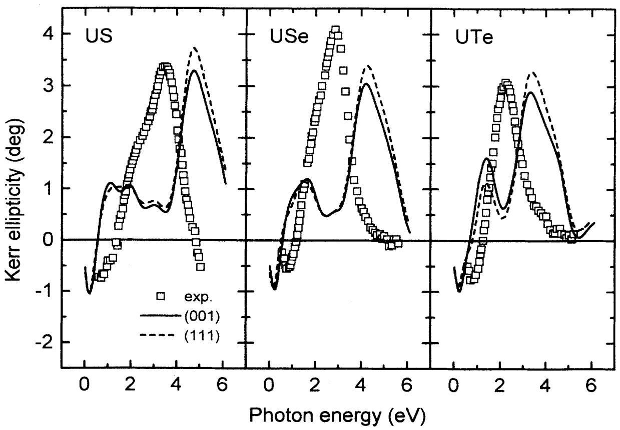

FIG. 2. As Fig. 1, but for the Kerr ellipticity spectra of US, USe, and UTe.

tween the theoretical and experimental spectra cannot be due to the nonpolar Kerr geometry used in the measurements.

To investigate the origin of the differences observed in the Kerr spectra, we consider the two components of the optical conductivity tensor, the diagonal and the off-diagonal components, which bring about the Kerr spectra [cf. Eq. (1)]. In this respect it is relevant to mention that both the off-diagonal conductivity and the diagonal conductivity were not measured directly.[10,11] The experimental diagonal conductivity was derived through a Kramers-Kronig transform of the measured reflectivity, whereas the off-diagonal conductivity has been calculated with Eq. (1) from the measured Kerr spectra and the diagonal conductivity. Therefore, the experimental optical spectra are not all independent. In Fig. 3 the theoretical and experimental real parts of the diagonal conductivities of the uranium monochalcogenides are displayed. Since these have been measured up to a higher energy than the Kerr spectra, we can now also compare the conductivity spectra in the energy range above 5 eV that were not treated by the Kerr spectra. With respect to the subscripts xx of σ in Fig. 3, we mention that these refer to directions relative to the uranium magnetization, which defines the z axis. Figure 3 shows that the agreement between the theoretical and experimental conductivity $\sigma_{xx}^{(1)}$ above 4 eV is rather satisfactory. Both the width and the height of the broad maximum at 6–8 eV are properly described by LSDA band-structure theory. In the lower-energy range of 0–4 eV, however, there are some marked differences between theory and experiment. Theory predicts two maxima of about the same height, whereas experiment gives one main peak at about 1 eV and a smaller shoulder at 1–2 eV. The experimental conductivities do, of course, contain an intraband contribution, which is not contained in the theoretical conductivity spectra. Adding a phenomenological intraband conductivity to the calculated interband conductivities would increase the total diagonal conductivity at low frequencies, in better agreement with experiment. But no realistic intraband conductivity added can eliminate the difference present. We anticipate that this difference relates to the one observed in the Kerr spectra. A careful analysis of the experimental conductivity spectra by Schoenes[10] showed that the second peak, which is clearly seen in the optical conductivity of US, is also present in those of USe and UTe. But with increasing mass of the chalcogenide atom this peak shifts to a lower energy and is simultaneously reduced in amplitude. In the theoretical spectra the second peak also shifts to a lower energy with increasing mass of the chalcogenide atom, but it is not reduced in height. In all three cases, the first theoretical maximum is smaller in height than the experimental value. The two peaks were assigned by Schoenes[10] to be due to $d \rightarrow f$ and $f \rightarrow d$ transitions. This would indicate that the LSDA description of the uranium f states plays a role in the differences between theoretical and experimental spectra. This will be discussed in more detail below.

To make a complete comparison for both the real and imaginary parts of the diagonal conductivity, we consider the reflectivity, which is a function of the real and imaginary parts (see Ref. 12). Results for the reflectivities are shown in Fig. 4. In the calculations of the reflectivities we used a smaller inverse lifetime of 0.2 eV, in order to display more clearly the fine structure of the spectra at low energies. Again the agreement with experiment is satisfactory, except for the reflectivities at about 10 eV, where theory predicts higher values. A bigger inverse lifetime would only be reasonable at these energies, and would thus yield a lower and smoother reflectivity at higher photon energies. Both the theoretical and experimental spectra show two peaks up to 5 eV, with the theoretical peak at 2–3 eV being higher than the experimental one. Apart from this, the reflectivities are in the lower-energy range reasonably described. Consequently, the real and also the imaginary parts of the diagonal conductivity are reasonably described by LSDA band-structure theory.

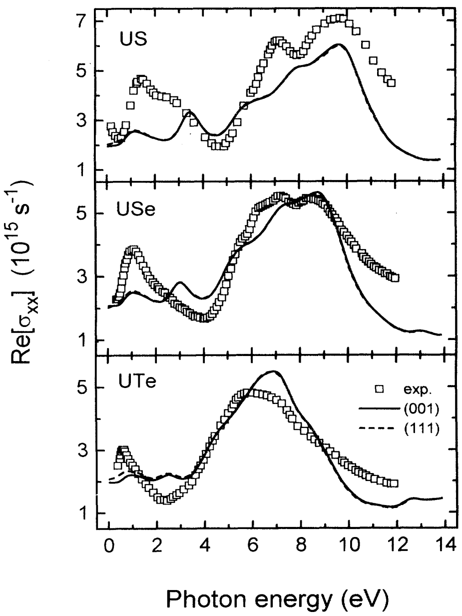

FIG. 3. Theoretical and experimental (Ref. 10) results for the absorptive part of the diagonal optical conductivity (Re[σ_{xx}]) of US, USe, and UTe. Aspects of the calculation are as given in the caption of Fig. 1.

Last, we compare the absorptive part of the off-diagonal conductivity, $\sigma_{xy}^{(2)}(\omega)$. These spectra are shown in Fig. 5. For US and USe we have scaled the experimental spectra down by a factor of 0.5. The experimental spectrum of UTe is unchanged. The reason for this magnitude difference is easily understood: The experimental $\sigma_{xy}^{(2)}(\omega)$ were calculated from the measured Kerr spectra and from the diagonal conductivity obtained from the reflectivity;[10] therefore the magnitude of the $\sigma_{xy}^{(2)}(\omega)$'s depends on the magnitude of the experimental diagonal conductivities, which are for US and USe almost 2 times larger than the theoretical diagonal conductivities, resulting thereby in an approximately 2 times larger off-diagonal conductivity. The difference in height is not necessarily borne out of an error in the theory, as the

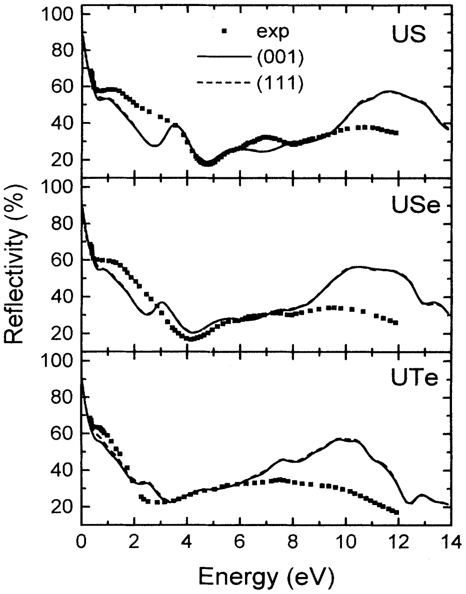

FIG. 4. Experimental (Ref. 10) and theoretical reflectivities of the uranium monochalcogenides. Theoretical reflectivities are computed with interband contributions only, given for the (001) and (111) orientations of the magnetization, and calculated with a relaxation-time broadening of 0.2 eV.

calculated Kerr spectra are of the same size as the experimental ones. Apart from the height of the optical conductivity spectra, it appears once more from Fig. 5 that theory predicts a double-peak structure, while experiment yields one large peak and only a smaller shoulder. Finding the origin of this difference would clarify what exactly is missing in the LSDA band-structure picture of the MO spectra of these compounds. This is studied further in the following section.

IV. ENERGY-BAND STRUCTURE

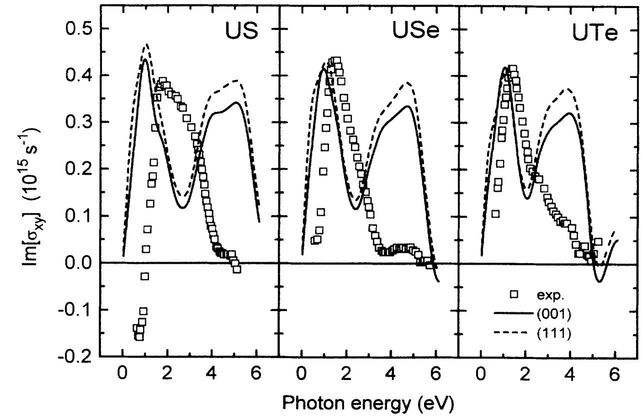

FIG. 5. As Fig. 3, but for the absorptive part of the off-diagonal conductivity ($\mathrm{Im}[\sigma_{xy}]$). The experimental off-diagonal conductivities (Ref. 10) of US and USe have been scaled down by a factor of 0.5.

For calculating the energy-band structures of the uranium chalcogenides we have used the scalar-relativistic ASW method[33] with SO coupling included through a second variation[34] as well as the fully relativistic LMTO method.[26] Two independent computational schemes were used in order to verify the reproducibility of the LSDA ground state. We found that the ground-state properties given by the two schemes are in excellent agreement. Also we recalculated the Kerr spectra using the fully relativistic LMTO method and a newly developed computational scheme for the optical transition-matrix elements for the LMTO method based on the Dirac equation, and which takes combined corrections into account.[27] The thus obtained Kerr spectra are found to be identical to those obtained with the ASW method, and are therefore not shown here. Previously, ground-state properties of one or two of these compounds were calculated using various methods by several authors.[7,13,16–18,37] The band structures of all three compounds were calculated by Brooks,[7] using the LMTO method based on the Pauli equation,[35] together with a SO term in a second variation. The more interesting quantities in the energy-band calculations are the spin and orbital magnetic moments, since these compounds are known to have very large orbital moments.[6,38] But it is also known that energy-band theory predicts total moments for the uranium chalcogenides of an itinerant situation that are substantially

TABLE I. Calculated and experimental magnetic moments of the (111) uranium monochalcogenides. Orbital moments are denoted by M_ℓ, spin moments by M_s, and total moments by M_{tot}. The moments pertaining to the chalcogenide atom are labeled with the superscript c and those pertaining to uranium with u. For comparison the f contributions to the moments (M^f) as calculated by Brooks (Ref. 7) are also included. The experimental moments were obtained through neutron-scattering experiments (M_{neut}) (Ref. 39), and bulk saturation-magnetization measurements (M_{sat}) (Refs. 3, 40, 41). The moments measured in neutron-scattering experiments are supposed to be close to the uranium f moment. All moments are given in μ_B.

	This work							Brooks (Ref. 7)		Experiment	
	M_s^c	M_ℓ^c	M_s^u	M_ℓ^u	M_{tot}	M_s^f	M_ℓ^f	M_s^f	M_ℓ^f	M_{sat}	M_{neut}
US	0.06	0.07	1.6	-2.5	-0.8	1.5	-2.6	2.1	-3.2	1.55	1.70 ± 0.03
USe	0.06	0.07	1.8	-2.8	-0.9	1.7	-2.9	2.4	-3.4	1.8	2.0 ± 0.1
UTe	0.08	0.08	2.2	-3.4	-1.0	2.0	-3.5	2.6	-3.4	1.9	2.2 ± 0.1

smaller than the experimental ones (see Ref. 38). In Table I we have collected results for the various magnetic moments of the uranium chalcogenides in (111) magnetization. Experimental moments have measured in neutron-scattering experiments[39] and in bulk saturation-magnetization measurements.[3,40,41] The saturation moment is always smaller than the moment obtained from neutron-scattering experiments, which is supposed to be close to the f-shell moment.[39] The f contribution of the moments obtained in this work are comparable to those computed by Brooks.[7] The f-spin moments in the present work are smaller than Brooks', but this might be due to a different choice of atomic sphere radii. In our calculations the atomic sphere radii have been chosen in such a manner that the charge transfer between uranium and the chalcogenide atom is negligible. We have obtained the same sphere radii also in another approach, by minimizing the Hartree energy with respect to the radii. As has been noted before, energy-band theory predicts for the uranium monochalcogenides a much too small total magnetic moment (cf. columns 6 and 11 in Table I). This stresses the necessity of an improvement of the LSDA ground-state description, possibly via an additional orbital polarization term in the Hamiltonian,[7,42,43] or through an LDA+U approach.[44] We do not give the theoretical moments for the (001) magnetization direction here, but only mention that the (001) uranium total moments are always 10–40 % smaller than those of the (111) direction. In addition we find from the calculated total energies that the (111) direction is the easy magnetization axis. Both findings are in accordance with saturation-magnetization measurements.[2,3,41]

The calculated band structures and density of states (DOS) are shown in Fig. 6. At the Fermi energy there is for all three monochalcogenides a high f density of states, placed in the middle of a broader d density. The other DOS visible below the Fermi energy are predominantly due to chalcogenide p and s bands. These results coincide with those of earlier molecular-cluster calculations.[37] Experimental investigations of the DOS in these compounds were previously carried out through photoemission measurements.[37,45] The electron-emission intensity of US measured by Erbudak and Meier[45] is shown in Fig. 7. Comparing this emission spectrum with the US DOS in Fig. 6 shows that there is good agreement: Up to 4 eV below the Fermi energy there are the uranium 5f and 6d states, and from 4 to 8 eV the sulfide valence p states. The sulfide s band, however, is experimentally at 10 eV, but theoretically at 15 eV below E_F. But because the s band is so deep below E_F, it can never contribute to the MO Kerr spectra. The positions of the energy bands that can contribute to the Kerr spectra are properly given by LSDA density-functional theory. Yet, subtle details of the positions of the f states near the Fermi energy cannot be in order; otherwise the theoretical moment would not deviate so much from the experimental one.

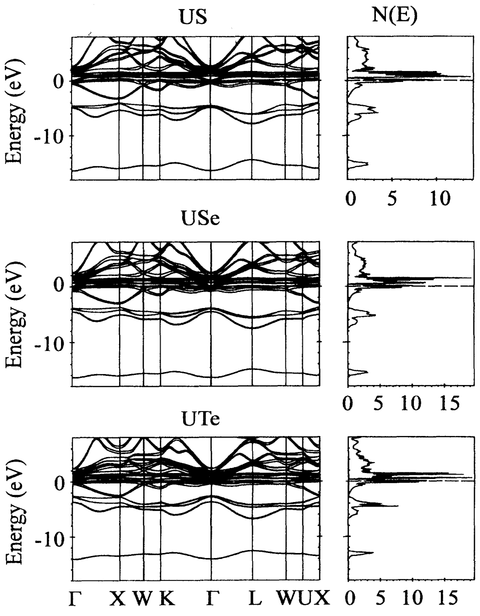

FIG. 6. Band structure (left-hand panel) and density of states (right-hand panel) of the (001) uranium monochalcogenides.

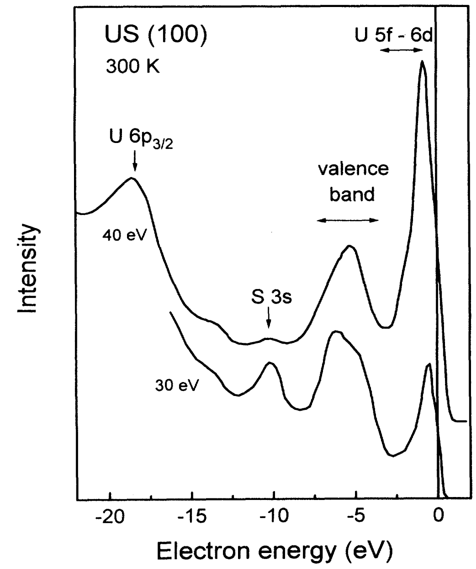

FIG. 7. Electron-emission intensity of US as measured by Erbudak and Meier (Ref. 45). The indicated positions of the bands may be compared with the DOS of US given in Fig. 6.

V. LATTICE SPACING AND EXTERNAL FIELD

In the preceding two sections it has been found that the gross features of the diagonal optical conductivity, reflectivity, and DOS are in accordance with experiment. The Kerr spectra, however, are especially sensitive to small changes in the energy bands that are caused by an interplay of exchange splitting and SO coupling. In view of the discrepancy between theoretical and measured moments, the latter quantities are not sufficiently well described. In an attempt to detect further what the reason for the difference between the experimental and theoretical Kerr spectra is, we consider the influence of the lattice spacing and of an applied magnetic field on the calculated Kerr spectra. Increasing the lattice spacing leads to a narrowing of the energy-band width and thus to a narrowing of the Kerr spectra (see, e.g., Ref. 46). This appears to be one of the things that is missing in the theoretical Kerr spectra, as these are all broader than the experimental ones (see Figs. 1, 2). Second, we consider the effect of an applied field on the Kerr spectra. Through an applied field we can change the spin and orbital moments, and thus simulate in an approximate way a different spin and orbital moment distribution.

In Figs. 8 and 9 we show first the effect of an increased lattice spacing on the Kerr spectra of the (001) magnetized monochalcogenides. The lattice constants have been increased by 3% and by 6%, respectively. As can be seen from Figs. 8, 9 the Kerr spectra do become more narrow, but even the already largely increased lattice constants of 6% larger are not enough to achieve the experimental width of the spectra. Neither does the double-peak structure in the Kerr spectra broaden to one wider peak. Remarkable, though, is the effect of the lattice constant on the magnetic moments. The orbital and spin moments on uranium increase considerably with increasing lattice constant: For (111) US the moments of the 6% larger lattice constant are $2.1\mu_B$ and $-3.2\mu_B$, for the uranium spin and orbital moments, respectively. For USe and UTe in (111) orientation, the uranium spin and orbital moments of the 6% larger lattice constant are $2.4\mu_B$, $-3.7\mu_B$, and $2.8\mu_B$, $-4.1\mu_B$, respectively. The moments on the chalcogenide atoms are practically unaffected. A similar behavior is obtained for the (001) orientation. Investigations of US under pressure showed that the magnetic moment decreases as a function of pressure,[47] consistent with the behavior obtained here from energy-band calculations. The uranium f states near the Fermi energy are thus particularly sensitive to the lattice constant, but this does not result in proportional changes in the Kerr spectra.

The magnetic moments can furthermore be changed by applying an external field. As a test, we have done this for USe in the (001) magnetization, using an unrealistically large field. The spin moments of uranium and Se become then much larger: $3.6\mu_B$ and $0.4\mu_B$, respectively, while the orbital moments are also a little bit larger: $-2.9\mu_B$, $0.08\mu_B$, for U and Se, respectively. The Kerr spectra calculated for (001) USe in applied field are shown in Fig. 10. The applied field has a substantial influence on the Kerr spectra, but the in-field Kerr spectra are in less good agreement with experiment than those without applied field. The present calculation surely does describe an exaggerated case; nevertheless, it does indicate that changing the magnetic moments does not necessarily lead to improved Kerr spectra. As a result of these tests, we find that it cannot be concluded that when the theoretical orbital and spin moments are equal to the experimental moment, the calculated Kerr spectra will also be in good agreement with the experimental ones.

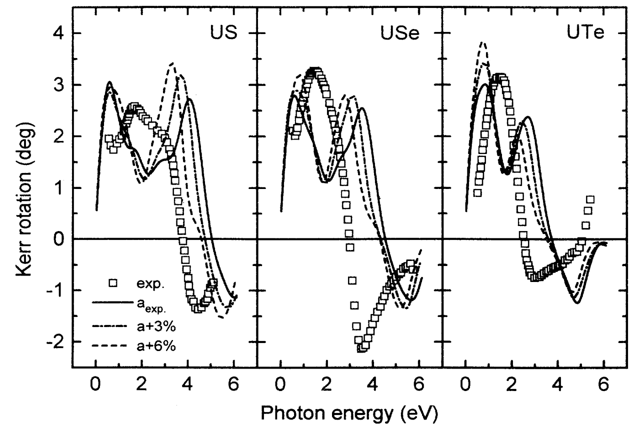

FIG. 8. Effect of the lattice spacing on the calculated Kerr rotation spectra of (001) US, USe, and UTe. Aspects of the calculation are as given in the caption of Fig. 1.

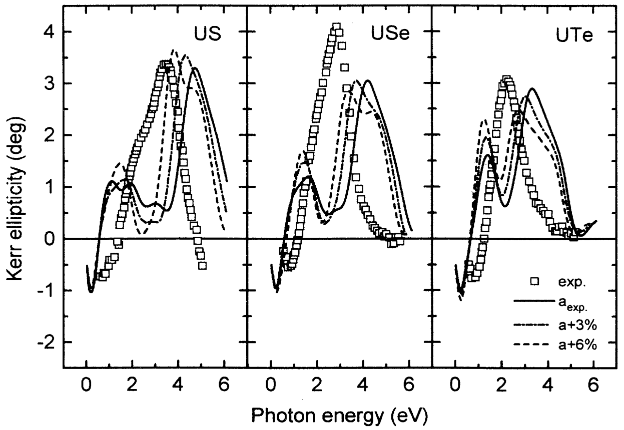

FIG. 9. As Fig. 8, but for the Kerr ellipticity spectra of (001) US, USe, and UTe.

VI. CONCLUSIONS AND DISCUSSION

The MO spectra of the uranium salts US, USe, and UTe have been studied with a relativistic LSDA band-structure approach. Several quantities, like the reflectivity, the diagonal conductivity ($\sigma_{xx}^{(1)}$), the preferred magnetization axis, and the positions of the energy bands, are in reasonable to good agreement with experimental data. Less good agreement has been obtained for the Kerr spectra and the magnetic moments. In particular, the shapes of the Kerr rotation and ellipticity spectra differ from experiment. We find that this difference is not due to missing relativistic corrections in the optical transition-matrix elements, and neither is it due to the nonpolar Kerr geometry used in the measurements. The calculated magnetic moments appear to be too small, but we find that tuning the size of the total moment does not correct the shape and magnitude of the *ab initio* Kerr spectra. In a strong applied field, the exchange splitting becomes much larger, which results in an altered Kerr spectrum, but not in an improvement with respect to experiment. The uranium $5f$ states are quite sensitive to the lattice constant, as is witnessed by considerable

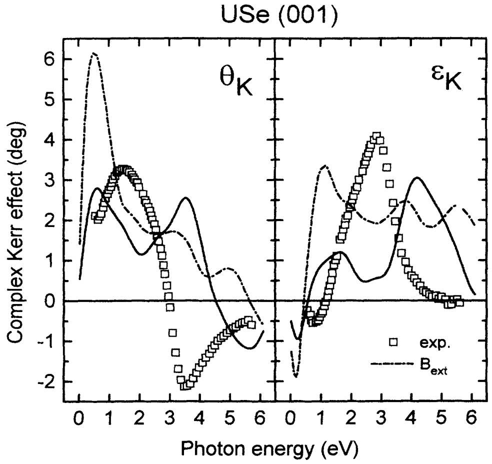

FIG. 10. Effect of an applied magnetic field on the calculated Kerr spectra of USe with (001) magnetization direction. The Kerr rotation is denoted by θ_K, and the Kerr ellipticity by ε_K.

changes of the magnetic moments. The *ab initio* Kerr spectra, however, do not show a similar sensitivity with respect to the lattice spacing. Therefore, it is unlikely that small deviations of the position of the $5f$ states with respect to experiment can account for the different shape of the first-principles Kerr spectra. These shape differences are, noticeably, only observed in those parts of the MO spectra, where transitions from the $5f$ states are involved. The optical spectra due to the $5f$ states are thus not sufficiently well described in the present energy-band approach.

Several schemes have been proposed to improve the LSDA band structure.[7,42–44] An orbital polarization term in the Hamiltonian has been introduced by Brooks,[7] Eriksson, Brooks, and Johansson,[42] and Severin, Brooks, and Johansson,[43] with the purpose to correct the LSDA magnetic moments. With an orbital polarization term added, the magnetic moments of US, USe, and UTe come into close correspondence with the experimental moments.[7,43] The Kerr spectra of US were recently calculated with an orbital polarization included by Gasche,[14] and Brooks, Gasche, and Johansson.[15] The resulting Kerr spectra, however, appear to deviate more from experiment than those presented in this work. Other calculations performed by Cooper and co-workers[16,17] for UTe with an orbital polarization term added gave a diagonal optical conductivity $\sigma_{xx}^{(1)}$ which is quite similar to ours. But for the off-diagonal conductivity those authors found that the orbital polarization failed to improve the theoretical description of the magneto-optics.[16] Therefore, it is at present premature to draw conclusions concerning the possible improvement that might be achieved by an orbital polarization. Another approach to treat the more localized f states is the so-called LDA+U method.[44] This method has recently been applied to the calculation of the optical conductivities of CeSb (Ref. 48) and Gd (Ref. 49). For both materials, this approach gives a reasonable to good agreement with experiment for the diagonal and off-diagonal parts of the optical conductivity. For CeSb, calculations of the conductivity spectra were also carried out by Lim, Price, and Cooper,[50] with an orbital polarization included. While the thus calculated diagonal optical conductivity is nearly identical to that of the LDA+U approach,[48] the off-diagonal LDA+U conductivity appears to represent the measured conductivity better in some parts of the spectrum. Thus, for CeSb the treatment of the $4f$ electrons and their electron correlation is the key to the appropriate description of the occurring physics.

It can be expected that this will be of importance too for the $5f$ electrons of uranium. The uranium $5f$ electrons, however, are more delocalized than the Ce $4f$ electrons, and, in these compounds, practically itinerant, with those of UTe possibly being quasilocalized (see, e.g., Refs. 47,51,52). Consequently, several ground-state properties are successfully predicted by LSDA band-structure theory. But optical transitions involving $5f$ states probe more specifically the electron correlation effects that are not included in the present LSDA band description. Improvements of the LSDA density-functional optical spectra of the uranium chalcogenides are therefore to be sought in an adequate treatment of the correlated electron behavior. Investigations in this direction are presently being undertaken.

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