Optical properties of U$_3$P$_4$

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Abstract

Optical and magneto-optical properties of the non-collinear ferromagnet U$_3$P$_4$ are studied theoretically over the broad energy range of 0–12 eV. The calculations are carried out in the framework of the local density functional theory treating the U 5f electrons as itinerant, and the results are compared with available experimental data. For low energies, below 5 eV, the agreement between theory and experiment is good. Above 5 eV, the theoretical optical characteristics exceed substantially the corresponding experimental values. Possible reasons for this difference are discussed. Much attention is devoted to the role played by the 5f electrons for the formation of the optical properties. To do this we determine the electronic structure and optical properties of Th$_3$P$_4$ which, although similar in many respects to U$_3$P$_4$, does not possess occupied 5f states. Our results for Th$_3$P$_4$ are compared with experimental data for Th$_3$P$_4$ and theoretical results for U$_3$P$_4$ in an attempt to relate the differences in the optical characteristics of both compounds to the effect of the U 5f electrons. By means of a model calculation we extract the contribution of the U 5f states to the optical properties of U$_3$P$_4$ and find this contribution to be substantial for energies below $E \approx 3$ eV. On the basis of good agreement between theory and experiment in this energy range we infer that in U$_3$P$_4$ the U 5f electrons are itinerant. Finally, we discuss the influence of the non-collinearity of the magnetic structure on the optical properties of U$_3$P$_4$.

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1. Introduction

Uranium compounds are very attractive objects for theoretical studies because they show a wide variety of physical properties. Thus, even compounds having the same crystal structure and similar composition can show remarkably different properties. Taking as an example the magnetic properties of the series of UT$_2$Si$_2$ compounds, where T is a 3d, 4d or 5d transition metal, one finds here (see, e.g., Ref. [1,2]) paramagnetic, ferromagnetic and antiferromagnetic compounds. Also more complex magnetic structures, non-collinear ferromagnetic [3], non-collinear antiferromagnetic...
and structures with periodicity incommensurate with the period of the crystal lattice, were reported. A number of compounds possess heavy-fermion properties and some are heavy-fermion superconductors.

Despite substantial efforts devoted to the study of these compounds during the past years, it is still not clear which physical mechanism determines their behavior. One of the central questions to be answered is, which of the two approaches, of localized 5f electrons or of itinerant 5f electrons, supplies a better basis for the discussion of the properties of this class of compounds? It is possible that no simple and unique answer explaining all compounds and all properties can be given to this question. Thus, for instance, for UPd$_3$, a good description of the position of the 5f states relative to the Fermi energy is likely to be supplied by the correlated impurity picture in contrast to the UT$_2$ (T is a 3d metal) series of compounds where the local approximation to spin-density-functional theory (LSDF), i.e., the itinerant electron picture, supplies a good description of the experimental properties.

In this situation, a special role is played by spectroscopic experiments because these supply the most direct information about the energy levels in question.

In the present paper, we wish to contribute to the study of the optical properties of U compounds. We selected U$_3$P$_4$ because it possesses a number of properties making it attractive for our purposes. First, our previous study of the ground-state magnetic structure revealed good agreement between theory and experiment. Second, good optical and magneto-optical experimental data is available. Third, the compound possesses an unusual non-collinear magnetic structure that raises an interesting question about the influence of the non-collinearity on the optical properties.

In a previous brief communication, we reported first results of calculations of the optical and magneto-optical properties of the non-collinear ferromagnet U$_3$P$_4$. The present paper contains the result of an extensive investigation of these properties. In particular, we extended the range of photon energies from 5 to 12 eV, carried out calculations for Th$_3$P$_4$ which, although in many respects similar to U$_3$P$_4$, does not contain occupied 5f states, studied the influence of the value of the relaxation time used in the calculations, and, finally investigated the orbital polarization enhancement on the optical properties. More attention is devoted to the relation between non-collinearity of the magnetic structure and the optical properties.

The paper is organized as follows. In Section 2, the calculational approach is briefly discussed. In Section 3, the results of the calculation of the optical and magneto-optical properties are presented and compared with experimental data. In Section 4, the role of the 5f electrons in U$_3$P$_4$ is elucidated by means of a comparison of the partial density of states and the optical conductivity spectra of U$_3$P$_4$ and Th$_3$P$_4$. An estimate is made of the contribution of the 5f states to the optical conductivity tensor employing a model calculation. In Section 5, the influence of the orbital polarization term on the diagonal and off-diagonal optical conductivity spectra is investigated. In Section 6, we report the optical and magneto-optical spectra of U$_3$P$_4$ calculated for various non-collinear magnetic configurations focusing particular attention on the different dependencies in the diagonal and off-diagonal components of the optical conductivity tensor.

2. Calculational approach

The optical properties of solids can be deduced from their optical conductivity tensor. Thus, the normal-incidence reflectivity is given, under certain symmetry requirements, by the diagonal component, $\sigma_{xx}$, of the optical conductivity tensor:

$$ R = \frac{(n - 1)^2 + k^2}{(n + 1)^2 + k^2}, \quad n + ik = \left(1 + \frac{4\pi\sigma_{xx}}{\omega}\right)^{1/2}, $$

(2.1)

where the $z$-axis is chosen to be perpendicular to the surface of the solid. To calculate the polar magneto-optical Kerr angle and ellipticity, both the diagonal and the off-diagonal components of the
the conductivity tensor are needed [16]
\[ \Phi_k = \text{Re} \left( \frac{-\sigma_{xy}}{\sigma_{xx} \sqrt{1 + 4\pi i/\omega \cdot \sigma_{xx}}} \right), \]
\[ \epsilon_k = \text{Im} \left( \frac{-\sigma_{xy}}{\sigma_{xx} \sqrt{1 + 4\pi i/\omega \cdot \sigma_{xx}}} \right) \] (2.2)

Here, the linearly polarized incident light wave is assumed to propagate along the \( z \)-axis and the electric field of the wave is supposed to be parallel to the \( x \)-axis.

Kubo’s theory [17] for the linear response gives in the random-phase approximation, the following expression for the elements of the conductivity tensor [18]
\[ \sigma_{xx}(\omega) = \frac{i e^2}{m^2 V} \sum_k \sum_{n,m} \left[ f(E_{k,n}) \cdot (1 - f(E_{k,m})) \left| (p_+|_{k,m,n})^2 + |(p_-|_{k,m,n})^2 \right. \right. \]
\[ \times \left. \left. \left( \frac{1}{\omega - E_{k,m} - E_{k,n} + i\delta} + \frac{1}{\omega - E_{k,n} - E_{k,m} + i\delta} \right) \right] \right. \]
\[ \sigma_{xy}(\omega) = \frac{e^2}{m^2 V} \sum_k \sum_{n,m} \left[ f(E_{k,n}) \cdot (1 - f(E_{k,m})) \left| (p_+|_{k,m,n})^2 - |(p_-|_{k,m,n})^2 \right. \right. \]
\[ \times \left. \left. \left( \frac{1}{\omega - E_{k,m} - E_{k,n} + i\delta} - \frac{1}{\omega - E_{k,n} - E_{k,m} + i\delta} \right) \right] \right. \] (2.3)

\[ \sigma_{xy}(\omega) = \frac{e^2}{m^2 V} \sum_k \sum_{n,m} \left[ f(E_{k,n}) \cdot (1 - f(E_{k,m})) \left| (p_+|_{k,m,n})^2 - |(p_-|_{k,m,n})^2 \right. \right. \]
\[ \times \left. \left. \left( \frac{1}{\omega - E_{k,m} - E_{k,n} + i\delta} - \frac{1}{\omega - E_{k,n} - E_{k,m} + i\delta} \right) \right] \right. \] (2.4)

where
\[ (p_+|_{k,m,n} = \langle k,m| p_x + i \cdot p_y |k,n \rangle, \]
\[ (p_-|_{k,m,n} = \langle k,m| p_x - i \cdot p_y |k,n \rangle \] (2.5)
denote matrix elements of components of the momentum operator and the quantities \( E_{k,n} \) are band energies. The matrix elements given by Eq. (2.5) determine the probabilities for electron transitions between the states, \((k, n) \) and \((k, m)\), induced by right and left circularly polarized light. The formulas Eq. (2.3) and Eq. (2.4) are valid for those cases where the symmetry group of the crystal possesses at least a threefold rotation or mirror-rotation axis about the \( z \)-axis [16]. The quantity \( \delta \) is a phenomenological parameter that accounts for finite lifetime effects.

In most of the calculations, the value of this parameter was chosen as \( \delta = 0.03 \text{ Ry} \), a value that was successfully used in a number of previous studies [19,20]. However, to exhibit the dependence of the theoretical results on \( \delta \), some calculations are repeated with \( \delta = 0.01 \text{ Ry} \).

The terms with equal band indices, \( n = m \), contribute to the intra-band part of the optical conductivity which can be represented as [21]
\[ \sigma_{\text{intra}}(\omega) = \frac{\sigma_{0,x}}{1 - i\omega \tau}, \]
\[ \sigma_{0,x} = \frac{\delta \omega^2_{\text{op}}}{4\pi}, \] (2.6)
\[ \delta \omega^2_{\text{op}} = \frac{4\pi e^2}{V} \sum_{k \in \text{BZ}} \delta(E_{k,n} - E_F) \cdot (v_x(k,n))^2, \]
\[ v_x(k,n) = \frac{1}{\hbar} \frac{\partial E_{k,n}}{\partial k_x}. \] (2.7)

Thus, the intra-band part of the conductivity depends sensitively on the plasma frequency which is determined by the properties of the electronic states at the Fermi level.

To calculate the electronic states, we use the augmented spherical waves (ASW) method [22] generalized to the case of non-collinear magnetic structures [23], incorporating spin–orbit coupling [11] and an effective orbital field correction [24]. The latter we write as
\[ \hat{H}_{\text{op}} = I_{\text{op}} L_z \cdot \hat{J}_z, \] (2.8)

thus taking into account interactions responsible for Hund’s second rule. Here \( L_z \) is the projection of the atomic orbital moment onto the local atomic \( z \)-axis. The parameter \( I_{\text{op}} \) was taken equal to 2.6 \( m\text{Ry} \) [24] and \( \hat{J}_z \) is the \( z \)-component of the angular momentum operator in the local frame of
reference. For a detailed discussion of the full Hamiltonian see Ref. [25].

3. Optical and magneto-optical properties of U₃P₄

U₃P₄ crystallizes in the Th₃P₄ structure which is defined by a BCC lattice and a basis of six uranium and eight phosphorus atoms (see e.g. Ref. [11]). In our calculations the experimental value of the lattice constant \( a = 15.4901a_0 \) [26] is used, \( a_0 \) being the Bohr radius. The radii of the atomic spheres, \( R_U = 3.500a_0 \) and \( R_P = 2.8560a_0 \), are chosen such that they result in approximate electro-neutrality of the atomic spheres.

It was first asserted by Buhrer [27] on the basis of magnetization data for a single crystal that U₃P₄ may have a non-collinear ferromagnetic structure. Przystawa and Praveczi [28] reported a theoretical study for U₃P₄ using a model Hamiltonian for localized spins, and finding, indeed, the ground-state magnetic structure to be non-collinear with a large ferromagnetic component along the [111]-axis. Neutron diffraction experiments [3] later confirmed this type of structure for U₃P₄.

In Ref. [11], a first-principles calculation of the magnetic structure in U₃P₄ was reported. On the basis of symmetry arguments, it was shown that the magnetic structure of this compound must be non-collinear revealing the importance of spin-orbit coupling for this effect. The calculated value of \( \mu_U = 1.36 \mu_B \) for the magnetic moment of the U atoms is in very good agreement with the experimental estimate of \( \mu_U = 1.37 \mu_B \). However, the value of the deviation of the atomic moments from the [111]-axis is calculated to be \( \theta = 1.4^\circ \) being much smaller than the experimental estimate of \( \theta = (13 \pm 6)^\circ \) [3]. Reasons for this difference can be found in both, the approximations inherent in the theory (e.g. the local density functional approximation), and the uncertainties in the evaluation of the experimental data. Concerning the latter we note that an investigation of the related compound U₃As₄ by the same authors [3] yields an even larger canting angle \( \theta \), a fact that is difficult to combine with the very small observed increase of the magnetization along the [111] direction obtained by applying an external magnetic field parallel to this axis [29]. The calculations reported in this section were carried out using the theoretical value of the canting angle.

Eq. (2.2) for the polar Kerr angle is applicable only in the case the magnetization axis (chosen as the z-axis) possesses at least threefold symmetry. The atomic positions and magnetic structure of U₃P₄ satisfy this condition: the magnetization is parallel to the crystallographic [111]-axis which is the threefold symmetry axis of the crystal. This symmetry stays intact also when the magnetic moments deviate from the [111]-axis forming a non-collinear cone structure [3,11]. Thus, by directing the z-axis along the crystallographic [111]-axis, we obtain the geometry necessary for the calculation of the polar magneto-optical Kerr rotation.

We begin with a comparison of the experimental and theoretical reflectivity spectra in Fig. 1. Below a photon energy of about \( E \approx 5 \) eV, the two curves are seen to agree well. However, for larger energies there is a substantial difference in the experimental and theoretical data. This could result from approximations in the theoretical approach in which low- and high-energy electron transitions are treated in the same way, although at different energies the relaxation processes might be quite different. In most of the calculations for optical properties of crystals that appeared so far the energy window used did not exceed the value of 6 eV [30,31]. Thus it seems possible that the validity of our theoretical approach for photon energies above 6 eV has not yet been established. Note, however, that good agreement of theory and experiment was obtained in a recent calculation [20] of the optical properties of US, USe and UTe in the energy interval 0–12 eV.

The deviation of the theoretical and experimental reflectivities may also have experimental reasons. It has been pointed out by the authors of the experimental paper [12] that the surface of the sample was polished; the resulting scratches and stress, it was suggested, can lead to a distinct reduction of the normal incidence reflectivity for energies larger than \( E \approx 5 \) eV. This is just the energy range where the theoretical values substantially exceed the experimental values. Another argument supporting the assumption that the difference of both curves above 5 eV might have experimental reasons is given by the analysis of the partial contributions
of the atomic states to the optical curves. As will be seen below, the part of the optical spectrum above 5 eV originates predominantly from electron transitions between valence states. This is in contrast to the energy region below 5 eV where the contribution of the U 5f states is important. The valence states are usually well described by the LDFT. Thus, it is natural to expect that the difference of the experimental and theoretical curves caused by the approximations in the theoretical scheme will appear in the low-energy part of the spectrum of the U$_3$P$_4$ compound and not above 5 eV.

Because of these uncertainties we devote our attention mainly to the low-energy part of the spectrum. At the same time, we hope that the present calculation of the optical spectra for the broad energy range will be a stimulus for further experimental studies.

On the right-hand-side of Fig. 1 we compare the experimental and theoretical diagonal conductivities. The experimental curve has been obtained by Schoenes et al. [12] from the experimental energy dependence of the reflectivity using a Kramers–Kronig transformation. Because of the integral character of the Kramers–Kronig transformation, the difference between the experimental and theoretical curves is expanded to a somewhat larger energy region and starts at the smaller energy of about 4 eV. Because of the large slope of the reflectivity curve for energies less than $E + 1$ eV, the Kramers–Kronig transformation in this region is very sensitive to the small variation of the spectrum. This can be the reason for the difference of the experimental and theoretical diagonal conductivities around 0.5 eV.

The calculation of the plasma frequency based on Eq. (2.7) results in a small value of $\omega_{p\parallel} \approx 0.72$ eV. Therefore, the calculated intra-band contribution to the diagonal optical conductivity, Eq. (2.6), is noticeable only for very low energies below 0.3 eV (see Fig. 1 where the intra-band contribution is shown). For a discussion of the curve labeled OPE here and in the next figure we refer to Section 5.

In Fig. 2, we compare the theoretical and experimental results for the real and imaginary parts of the off-diagonal component of the conductivity tensor. Theory and experiment are in reasonably good

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Fig. 1. Photon energy dependence of the normal-incidence reflectivity $R$ (left) and the real diagonal optical conductivity (right) of U$_3$P$_4$ compared with experimental data of Schoenes et al. [12]. The calculations were carried out for two values of the broadening parameter, $\delta = 0.03$ Ry and $\delta = 0.01$ Ry. The intra-band contribution to Re $\sigma_{xx}$ and the optical conductivity calculated without orbital polarization enhancement (OPE) are also shown.
agreement especially concerning general trends and the form of the strong peak in the low-energy region of both spectra.

We may comment on a previous phenomenological calculation [13]. By introducing four adjustable parameters, Reim [13] succeeded in reproducing approximately the experimental off-diagonal conductivity using the so-called screw-scattering model for intra-band transitions suggested by Erskine and Stern [32,33]. However, the value of the plasma frequency needed for one of the adjustable parameters was \( \hbar \omega_{\text{pl}} \approx 4.2 \text{ eV} \), which is much larger than the result of our calculation. The good agreement of our results with the experimental data exposes the inter-band transitions to play the primary role in the formation of the off-diagonal optical conductivity.

The Kerr spectra calculated on the basis of the diagonal and off-diagonal conductivity are graphed in Fig. 3. Comparison with the experimental spectra (Fig. 3) shows rather good agreement between the theoretical curves obtained for the standard value of the lifetime parameter, \( \delta = 0.03 \text{ Ry} \), and the experimental data [13]. Thus the position of the main low-energy peak and the general trend in the energy dependence of the spectra are well reproduced by the calculation. To judge the importance of the lifetime parameter \( \delta \), we also show results that are obtained by using the smaller value of \( \delta = 0.01 \text{ Ry} \).

Summarizing, there is good agreement between the theoretical and experimental optical spectra in the energy range up to \( E \approx 5 \text{ eV} \). We next attempt to reveal the role of the \( \text{U} \) \( 5f \) electrons in the formation of the optical spectra of \( \text{U}_3\text{P}_4 \).

4. Role of the \( 5f \) electrons in the optical properties

One possible way to expose the role of the \( 5f \) electrons in the formation of the optical properties of \( \text{U}_3\text{P}_4 \) was suggested by Schoenes et al. [12]. They compared the experimental optical spectra of \( \text{U}_3\text{P}_4 \) with those of \( \text{Th}_3\text{P}_4 \) and assumed that the difference between them can be explained by the influence of the \( 5f \) electron states occupied in the \( \text{U} \) compound but not in the \( \text{Th} \) compound. Although the number of the \( 5f \) electrons is not the only difference between both compounds, e.g. the \( \text{Th} \) atom has one additional \( 6d \) electron and the
lattice parameters of both compounds are different, this assumption seems to supply a good basis for a qualitative analysis of the two spectra. Indeed, Schoenes et al. [12] noticed an almost rigid shift of $\Delta E \approx 0.85$ eV between the structural elements of both optical spectra. The optical transitions were supposed to take place mostly between P p and Me d states where Me denotes Th or U. This shift in the optical spectra was assumed to be caused by the hybridization of the localized 5f U states with the valence P p states resulting in a shift of the P p states to higher energies in the case of U$_3$P$_4$. Another consequence of the assumed hybridization shift is the closing of an energy gap between empty and occupied states [12], Th$_3$P$_4$ being an insulator in contrast to U$_3$P$_4$ which is a low conductivity metal.

Thus we carry out calculations of the electronic structure and optical properties of Th$_3$P$_4$ and compare them with the corresponding results for U$_3$P$_4$, using for Th$_3$P$_4$ a lattice constant of $a = 16.2838 \alpha_0$ and atomic sphere radii of $R_{\text{P}} = 2.8562 \alpha_0$ and $R_{\text{Th}} = 3.79912 \alpha_0$ [26].

We begin with a brief description of the results for Th$_3$P$_4$ and show in Fig. 4 the density of states (DOS) of Th$_3$P$_4$ separating the partial DOS of the U 5f electrons from the remaining contributions. In agreement with experiment, the ground state of Th$_3$P$_4$ is found to be non-magnetic. Therefore, the partial spin-up and spin-down DOS are identical. Another important feature of the theoretical DOS is the clearly visible tendency of the formation of an energy gap at the Fermi edge, $E_F$, which separates occupied states of predominantly P 3p character from unoccupied states of mostly Th 6d character. But there is a very small energy overlap of the theoretical valence and conduction bands resulting in a finite DOS at the Fermi level. Note, that the presence of a finite number of electron states at the Fermi level is not in agreement with the conclusion of Schoenes et al. [12] about an indirect gap of $\Delta E \approx 0.4$ eV. A possible explanation for this discrepancy is the well known failure of the LDFT to correctly predict semiconducting energy gaps. But also there are uncertainties in estimating the gap from experimental data, for which the energy dependence of the absorption coefficient was fitted with a formula based essentially on an approximate account for electron transitions involving emission or absorption of phonons. Note, that our calculation gives rather good agreement between theory and experiment for the low-energy part of the
off-diagonal optical conductivity spectra (Fig. 2) without taking these kinds of transitions into account. As a result, we obtain the same estimate of $\Delta E \approx 0.4 \text{ eV}$ but in our case for the direct gap. For this estimate we implicitly assume that transitions involving the emission or absorption of phonons have much lower probability than the direct transitions taken into account in Eqs. (2.3) and (2.4). For a calculation in which indirect electron transitions are properly treated, one needs reliable information about the phonon spectrum that is not presently available for Th$_3$P$_4$.

The experimental and theoretical reflectivities of Th$_3$P$_4$ are compared in Fig. 5. The lifetime parameter is set equal to $\delta = 0.01 \text{ Ry}$ except for the energy region below $E = 0.7 \text{ eV}$, where a smaller value of $\delta = 0.001 \text{ Ry}$ has been used to better describe the effects of the formation of the direct gap between occupied and empty states. As in the case of U$_3$P$_4$ the agreement between theory and experiment is much better for energies in the interval 0–6 eV than for higher energies (see discussion above).

The structure of the spectra is exposed more clearly in the diagonal optical conductivity shown

Fig. 4. Partial density of states (DOS) of Th$_3$P$_4$. The spin-resolved 5f DOS is shown on the right-hand side. On the left-hand side the total DOS is shown minus that of the 5f electrons. The states supplying the main contribution to the DOS in different energy intervals are shaded.

Fig. 5. Comparison of experimental [12] and theoretical normal-incidence reflectivity spectra of Th$_3$P$_4$. The theoretical spectrum has been calculated with a broadening parameter of $\delta = 0.01 \text{ Ry}$. In the energy region below $E \approx 0.7 \text{ eV}$ a smaller value of $\delta = 0.001 \text{ Ry}$ has been used to better describe the effects of the formation of the direct gap between occupied and empty states.
Fig. 6. Comparison of the real diagonal optical conductivity spectra of \( \text{U}_3\text{P}_4 \) and \( \text{Th}_3\text{P}_4 \). On the left-hand side the theoretical spectra and on the right-hand side the experimental results of Schoenes et al. [12] are shown. To preserve the edge-form of the spectra the smoothing parameter \( \delta \) has been put equal to zero at energies below 0.7 eV. Following the treatment of the experimental curves by Schoenes et al. [12], we mark with arrows possible relations between structure elements of the theoretical conductivity of \( \text{U}_3\text{P}_4 \) and \( \text{Th}_3\text{P}_4 \).

in Fig. 6. To preserve the edge-form of the spectra the parameter \( \delta \) has been put equal to zero at energies below 0.7 eV. Comparing the diagonal conductivities of \( \text{Th}_3\text{P}_4 \) and \( \text{U}_3\text{P}_4 \), we see that the theoretical and experimental data have the following features in common. First, at low energies, there is a striking difference between the optical spectra of \( \text{Th}_3\text{P}_4 \) and \( \text{U}_3\text{P}_4 \); the former showing clearly the presence of an energy edge. Second, there are intersections of the curves at energies of about 2.5 and 5 eV. Between these energies, the conductivity of \( \text{Th}_3\text{P}_4 \) exceeds that of \( \text{U}_3\text{P}_4 \) being smaller otherwise. Third, although not very distinctly evident, there is a common structure of the theoretical and experimental curves. We now attempt to gain some understanding of these features on the basis of the calculated electronic structure paying special attention to the role of the U 5f states.

The first feature, the edge-type behavior in \( \text{Th}_3\text{P}_4 \), is evidently related to the gap between P 3p and Th 6d states. There are two reasons for the closure of this gap in \( \text{U}_3\text{P}_4 \), both being directly related to the 5f U states. First, as can be seen in Fig. 7, the U 5f states lie in an energy interval which overlaps the upper part of the P p states and the lower part of the U 6d states. Second, the DOS of the valence electrons also possesses no gap in the case of \( \text{U}_3\text{P}_4 \) (Fig. 7). In Fig. 7 we clearly see that the reason for closing the gap in the DOS of the valence electrons is the spin-polarization of the U 6d states as a result of which the spin-up states are shifted to lower energies approaching the P p states. This spin-polarization which is induced by the strong spin-polarization of the U 5f states was not taken into account in the qualitative scheme of Schoenes et al. [12].

The second feature, the relative values of the optical conductivities in different energy intervals, at low energies is directly related to the edge-type behavior of the conductivity of \( \text{Th}_3\text{P}_4 \) discussed above. Also the contribution of the electron transitions involving the U 5f states in this energy interval is substantial. This is clearly shown with the model calculation discussed below (see Fig. 8 and the corresponding discussion). However, it is not easy to find a simple explanation of the relation between the optical conductivities of \( \text{U}_3\text{P}_4 \) and \( \text{Th}_3\text{P}_4 \) for energies above 2.5 eV. It is the result of the complexity of the electron structures of the compounds which allow various electron transitions for the same photon energy. Here we suggest one possible interpretation of the observed features. This interpretation is based on the analysis of the DOS.
In Fig. 4, it is seen that three distinct peaks of the Th 6d-DOS in the energy interval 0–4 eV are replaced in the case of $U_3P_4$ by a somewhat decreased U 6d-DOS with numerous small peaks. This change of the DOS is due to hybridization between the U 5f and U 6d states. This effect influences the number and the probability of the electron transitions between the occupied P 3p states and empty U 6d states and may be responsible for the lower optical conductivity of $U_3P_4$ in the interval of photon energies between 2.5 and of 5 eV. Note, that the transitions to the empty Th 5f states, although of smaller probability, also contribute to this energy interval increasing the optical conductivity of $Th_3P_4$. 

Fig. 7. Partial density of states (DOS) of $U_3P_4$. The spin-resolved 5f DOS is shown on the right-hand side. On the left-hand side the total DOS is shown minus that of the 5f electrons. The states supplying the main contribution to the DOS in different energy intervals are shaded.

Fig. 8. Photon energy dependence of the real part of the diagonal (left) and imaginary part of the off-diagonal component of the optical conductivity tensor (right) of $U_3P_4$. Also the curves calculated without the contribution of the U 5f states are shown.
The higher value of the optical conductivity of \( \text{U}_3\text{P}_4 \) above 5 eV we relate to the larger width of the U 6d bands compared to the Th 6d bands. Indeed, the U 6d peaks at about 8.5 eV are shifted noticeably to higher energies compared to the corresponding peak of the Th 6d states at 7.5 eV (Fig. 4 and Fig. 7). The increased energy distance between the P p states and the upper part of the 6d bands explains the observed increase of the optical conductivity at the corresponding energies. Note, that we deal with the broadening of the U 6d bands compared with the Th 6d bands and not with the relative shift of all 6d states because some of the features of the DOS assume equal energy positions (e.g. the peak at 2.5 eV) or are even shifted in the opposite direction (e.g. the bottom of the 6d bands).

The shift of the bottom part of the U 6d states to lower energies compared to Th 6d states is in good correlation with the experimental observation \[12\] of the shift of some structural elements of the optical spectra to lower energies in the case of \( \text{U}_3\text{P}_4 \).

We may summarize this section by stating that comparing data for \( \text{U}_3\text{P}_4 \) and \( \text{Th}_3\text{P}_4 \) is of definite physical interest but yields only limited information on the nature of the 5f electrons and the role they play in the formation of the optical properties. To obtain more direct information about these questions we repeat the calculation of the frequency dependent optical conductivity tensor neglecting the contributions of the U 5f states entirely. To do this, all electron-eigenvalues \( E_{n\lambda} \) were left unchanged, but in the electron eigenfunctions, which are linear combinations of different atomic-like basis functions \[34\], the coefficients responsible for the U 5f contribution were set equal to zero. The diagonal and off-diagonal parts of the optical conductivity tensor calculated this way are compared with those that include all states (denoted by total) in Fig. 8.

The drastic differences in the energy region below 5 eV, especially in the off-diagonal conductivity are quite striking and demonstrate clearly the important role of the 5f electrons in determining the optical spectrum in this energy interval. For energies above 5 eV, the U 5f states are less important.

5. Orbital polarization enhancement

In all the calculations discussed above, the Hamiltonian of the problem contains the orbital-polarization-enhancement (OPE) term, Eq. (2.8). This correction to the usual Hamiltonian of the LDFT was suggested \[24\] in order to take into account interactions responsible for Hund's second rule and leads to a substantial increase of the orbital moment of the U atoms. In the case of \( \text{U}_3\text{P}_4 \), inclusion of the OPE term leads \[11\] to very good agreement between theory and experiment concerning the value of the magnetic moment of the U atoms. Without the OPE term the self-consistent orbital moment decreases from 3.08 to 1.79\( \mu_B \). Although the oppositely directed spin moment decreases as well from 1.72 to 1.39\( \mu_B \), this decrease is much smaller and cannot compensate the change of the orbital moment. Hence, the total moment of the U atom decreases substantially below the experimental value.

Although the OPE term is widely used in calculations of the magnetic properties of Actinide compounds, its influence on the optical properties has not yet been studied. In Figs. 1 and 2, we compare the optical data calculated with and without the OPE term. Since in both calculations the same spin-polarized potential is used, the differences seen must be entirely due to the OPE term. Thus the real part of the diagonal conductivity is seen to depend only weakly on the OPE correction. The difference between both theoretical curves is seen to be noticeable only in the low-energy part of the spectrum up to about 2 eV. In this region the calculation without the OPE correction results in somewhat better agreement with experiment. This concerns the description of the minimum of \( \text{Re} \sigma_{xx} \) at low photon energies and of the shoulder at energies about 1 eV. This shoulder is clearly seen in the experiment and is well reproduced in the calculation without the OPE correction.

The results for \( \text{Im} \sigma_{xy} \), Fig. 2, seem to confirm this tendency. In this case, neglecting the OPE correction one obtains a better description of the main peak of the experimental curve at about 1 eV. However, further studies are needed for a variety of compounds to assess with certainty the role of OPE corrections in theoretical investigations of optical spectra.
6. Optical properties and non-collinearity of the magnetic structure

As was mentioned in Section 3, there is a substantial discrepancy between theoretical, $\theta = 1.4^\circ$, and experimental, $\theta = (13 \pm 6)^\circ$, estimates of the canting angle $\theta$. This discrepancy stimulated us to study the dependence of the optical properties on $\theta$. In the case of a strong dependence of the theoretical optical spectra on $\theta$, a comparison of the experimental and theoretical data could give an independent estimate of the canting angle. Another, more important reason for investigating the dependence of the electron properties on the canting angle is the temperature dependence of the angles between the atomic magnetic moments. In the Heisenberg theory of localized moments one of the main parameters describing the state of a ferromagnet at finite temperatures is the average value of $\cos \phi$ where $\phi$ is the angle between neighboring atomic moments. In contrast to the Heisenberg theory, the thermodynamics of itinerant electron ferromagnets was initially supposed to be well described by the Stoner theory.

Stoner’s approach is based on the assumption that heating of a ferromagnet, basically because of electron transitions to the Stoner continuum, results in the decrease of the length of the atomic magnetic moments which, however, keep their parallel directions. Therefore, Stoner’s theory treats the state above the Curie temperature as non-magnetic, i.e. not only the global magnetic moment but also the local magnetization is supposed to be zero.

But this simple approach is no longer considered to be correct. Numerous problems of Stoner’s theory have been overcome by a number of theoretical developments, which, although treating the magnetic electrons as itinerant, allow for the fluctuations of the direction of the local magnetization [35]. This development made the LDFT of non-collinear magnetic structures an important part of the theory of magnetism at finite temperatures [36].

A quantitative theory of the temperature properties of a system must include the statistical-mechanics averaging over the states of the system. For any condensed system, such averaging is a complicated mathematical problem and cannot be carried out without serious approximations, even for the elementary 3d metals. However, already a detailed study of selected non-collinear excited states of the system may supply interesting qualitative information about the properties of this system [37,38]. This qualitative approach has been used here.

For the above mentioned reasons, we carry out calculations of the electron structure and optical properties of U$_3$P$_4$ for a number of non-collinear magnetic configurations with different values of the canting angle $\theta$ in the interval from $1.4^\circ$ up to $90^\circ$. In contrast to the usual LDFT calculations where the magnetic moments move during the calculation tending to assume the positions with minimal total energy, these, so-called constrained calculations have been carried out for a value of the $\theta$ angle kept unchanged during the calculations.

The so determined $\text{Re } \sigma_{xx}$ and $\text{Im } \sigma_{xy}$ spectra are shown in Fig. 9 for different values of $\theta$. The dependence of $\text{Re } \sigma_{xx}$ on the canting angle is seen to be surprisingly weak whereas the energy dependence of $\text{Im } \sigma_{xy}$ and the Kerr rotation (Fig. 10) practically scales (right-hand side of Fig. 10) with the value of $\cos \theta$. We particularly note that our calculations give values of the local magnetic moment of the U atoms that are, to a very good approximation, independent of the relative orientation. Thus the scaling factor $\cos \theta$ is proportional to the macroscopic magnetization that is given by the projection of the magnetic moments onto the [111]-axis as a scaling factor. We see, however, that for small angles the change of the optical response with angle is very small so that, unfortunately, it is not possible to determine the actual canting angle by comparing the theoretical and experimental spectra.

To understand the conspicuous difference between the angular dependence of $\text{Re } \sigma_{xx}$ and $\text{Im } \sigma_{xy}$ we observe that, although the same electron transitions contribute to both components, the weight of the contributions is different [16]: the absorption part of the diagonal component can be represented as a sum of components for right and left circularly polarized light

\[
|\langle b|p_+|a\rangle|^2 = |\langle b|p_y|a\rangle|^2
= \frac{1}{4}( |\langle b|p_+|a\rangle|^2 + |\langle b|p_-|a\rangle|^2),
\]  

(6.1)
in contrast to the absorption part of the off-diagonal component which can be represented as a difference of the corresponding characteristics for right and left circularly polarized light

\[ \langle b | p_x | a \rangle \langle a | p_y | b \rangle = \frac{i}{4} (| \langle b | p_+ | a \rangle |^2 - | \langle b | p_- | a \rangle |^2). \]  

(6.2)

Here, \( | a \rangle = | k, n \rangle \) and \( | b \rangle = | k, m \rangle \) are initial and final electron states.

As a direct consequence of this property the off-diagonal component of the conductivity tensor must be zero in the case when the right and left circularly polarized waves become equivalent. This condition is practically fulfilled in the calculation with \( \theta = 90^\circ \), which leads to very low values for the \( \text{Im} \sigma_{xy} \) spectrum and the Kerr angle. We note, that in the case of \( U_3P_4 \) we do not obtain an exactly vanishing Kerr rotation because the \( xy \)-plane is not a symmetry plane and therefore the right and left circularly
polarized waves are not exactly equivalent even for \( \theta = 90^\circ \).

Thus, the monotonic decrease of the Kerr rotation with increasing canting angle that is obtained in our calculations can be seen to be a natural consequence of the decreasing difference between the optical response to right and left circularly polarized light waves. Still, the insensitivity of the Re \( \sigma_{xx} \) spectrum to canting and the simple scaling of the Im \( \sigma_{xy} \) spectrum and the Kerr rotation peak with respect to the \( z \)-projection of the magnetic moment are non-trivial. The weak dependence of the diagonal component of the conductivity tensor on the magnetic structure can be interpreted as follows. The electron states enter the optical conductivity through the eigenenergies and the matrix elements involving the eigenfunctions, both of which can thus depend only weakly on the change of the directions of the atomic moments. This means, first, that the U 5f states, as seen in the local atomic coordinate system having the quantization axis parallel to the atomic moment, are almost unchanged for any magnetic configuration. Second, the hybridization of the U 5f states with the non-magnetic valence states, e.g. the P 3p states, does not change substantially with rotation of the U 5f states. This results in the weak dependence of the energy values and near invariance of the transition probabilities.

To understand the observed dependence of the optical spectra more quantitatively we consider a simple model and calculate the optical spectra of three isolated magnetic U atoms. To preserve the three-fold symmetry necessary for the simple form of the conductivity tensor Eqs. (2.3) and (2.4) we assume that the directions of the magnetic moments of the atoms are defined by the same value of the angle \( \theta \) and the following values of \( \phi \): 0°, 120° and 240°, respectively for the first, second and third atom. In agreement with our qualitative analysis we assume that the atomic wave functions taken in the local system of the atom do not depend on the direction of the moment. Then, transforming the components of the momentum operator from the global coordinate system to the local atomic systems we get, after some algebra, the following expressions for the combinations of the transition matrix elements entering the relations for \( \sigma_{xx} \) and \( \sigma_{xy} \)

\[
|\langle p_+ \rangle|^2 + |\langle p_- \rangle|^2 \propto 2 \cdot |\langle b | p_3 | a \rangle|^2 + \sin^2 \theta \cdot (|\langle b | p_3 | a \rangle|^2 - |\langle b | p_1 | a \rangle|^2) + \sin \theta \cdot \cos \theta \cdot (\langle b | p_3 | a \rangle \langle a | p_3 | b \rangle + \langle b | p_3 | a \rangle \langle a | p_3 | b \rangle), \tag{6.3}
\]

\[
|\langle p_+ \rangle|^2 - |\langle p_- \rangle|^2 \propto \cos \theta \cdot (\langle b | p_3 | a \rangle \langle a | p_3 | b \rangle - \langle b | p_3 | a \rangle \langle a | p_3 | b \rangle). \tag{6.4}
\]

Note, that all matrix elements in Eqs. (6.3) and (6.4) are written in the local atomic systems and are independent of the angle \( \theta \).

The following arguments allow us to treat the products \( \langle b | p_3 | a \rangle \langle a | p_3 | b \rangle \) and \( \langle b | p_3 | a \rangle \langle a | p_3 | b \rangle \) as small. In terms of spherical harmonics, \( Y_{lm} \), the two factors of each product are characterized by different selection rules: \( \Delta m = 0 \) for the \( \langle a | p_3 | b \rangle \) and \( \Delta m = \pm 1 \) for the \( \langle b | p_3 | a \rangle \) and \( \langle b | p_3 | a \rangle \) matrix elements. Although the spin-orbit coupling destroys \( m \) as a good quantum number of the atomic eigenstates, for every component of the spinor eigenfunction we still can determine the value of \( m \) supplying the main contribution. Because the operators \( p_\pi, p_\rho \) and \( p_\sigma \) do not mix the spinor components with different spin projections the \( \langle b | p_3 | a \rangle \langle a | p_3 | b \rangle \) and \( \langle b | p_3 | a \rangle \langle a | p_3 | b \rangle \) terms in Eqs. (6.3) and (6.4) are smaller than the other terms and may be neglected in our qualitative treatment. Eq. (6.4) then gives the proportionality between Im \( \sigma_{xy} \) and \( \cos \theta \) which is in very good correspondence with our LDFT calculations for U\(_3\)P\(_4\) (Fig. 9).

To understand the weak angle-dependence of the Re \( \sigma_{xx} \) spectrum, note that the term \( |\langle b | p_3 | a \rangle|^2 - |\langle b | p_3 | a \rangle|^2 \) determining the angle-dependence of Re \( \sigma_{xx} \) in our model describes the deviation of the atom from spherically symmetric form. For the case this deviation can be neglected we obtain values of Re \( \sigma_{xx} \) independent of \( \theta \).

Thus, the study of this simple model supports distinctly our conclusion that the angle dependence of the optical spectra of U\(_3\)P\(_4\) can be qualitatively interpreted in terms of a well-defined atomic moment of the U atoms which in our theory is formed.
by itinerant 5f electrons. Correspondingly, the effect of temperature must be treated in terms of disordering of the atomic moments and not in Stoner’s picture of decreasing local magnetization.

7. Conclusions

Optical and magneto-optical properties of the non-collinear ferromagnet $\text{U}_3\text{P}_4$ were studied theoretically in the broad energy interval of $0$–$12\text{ eV}$. Calculations were carried out in the framework of the local density functional theory treating the U 5f electrons as itinerant. The results of the calculations are compared with available experimental data. For energies below $5\text{ eV}$, we obtain rather good agreement between theory and experiment. Above $5\text{ eV}$, the theoretical optical characteristics exceed substantially the corresponding experimental values. The reasons for this difference are discussed. Much attention is devoted to the role of the 5f electrons in the formation of the optical properties. Following Schoenes et al. [12] we studied the electron structure and optical properties of the $\text{Th}_3\text{P}_4$ compound which, although similar in many respects to $\text{U}_3\text{P}_4$, does not possess occupied 5f states. Results of calculations for $\text{Th}_3\text{P}_4$ are compared with experimental data for $\text{Th}_3\text{P}_4$ and theoretical results for $\text{U}_3\text{P}_4$. We attempt to relate the difference between optical characteristics of both compounds to the effect of the U 5f electrons. By means of a model calculation we studied directly the contribution of the U 5f states to the optical properties of $\text{U}_3\text{P}_4$. We found this contribution being substantial for energies below $E \approx 3\text{ eV}$. On the basis of good agreement between theory and experiment in this energy range we draw the conclusion about the itinerant nature of the U 5f electrons in $\text{U}_3\text{P}_4$. We discuss the influence of the non-collinearity of the magnetic structure on the optical properties of $\text{U}_3\text{P}_4$ and contrast the weak dependence of the diagonal conductivity with the strong dependence of the off-diagonal conductivity on the magnetic configuration. We conclude that the magnetism of this compound can be described in terms of well-defined local moments of the U atoms that are formed by itinerant U 5f electrons.

We hope that the present attempt of a critical comparison of theoretical and experimental data for optical properties of $\text{U}_3\text{P}_4$ will stimulate further studies of this interesting compound.

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