

Electronic structure and magneto-optical Kerr effect in UCuAs₂

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The optical and magneto-optical (MO) spectra of the ternary compound UCuAs₂ are investigated theoretically from first principles, using the fully relativistic Dirac linear-muffin-tin-orbital band structure method. The electronic structure is obtained with the local spin-density approximation (LSDA), as well as with the so-called LSDA+*U* approach. Better agreement between the theoretically calculated and the experimentally measured MO Kerr spectra is found with the LSDA+*U* approximation. The origin of the Kerr rotation in the compound is examined.

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1. Introduction

Determination of the energy band structure of solids is a many-body problem. Band theory (a mean-field theory for treating this problem) in the framework of the local spin-density approximation (LSDA) has been successful for many kinds of materials and has become an exceptionally valuable tool for first-principles calculations in solid state physics. However, there are some systematic errors which have been observed when using the LSDA. In particular, the LSDA fails to describe the electronic structure and properties of *4f* and some *5f* electron systems in which the on-site Coulomb interaction among the electrons is strong. A wide variety of physical properties arise from the correlations among *f* electrons in these materials: metal–insulator transitions, valence fluctuations in the Kondo effect, heavy fermion behavior, superconductivity, and so on. Such materials are called

strongly correlated electron systems. Many new concepts for addressing these phenomena have been proposed, and this is a field of very active research.

Actinide compounds occupy an intermediate position between itinerant *3d* and localized *4f* systems [1,2], and one of the fundamental questions concerning actinide materials is whether their *5f* states are localized or itinerant. This question is most frequently answered by comparison between experimental spectroscopies and the different theoretical descriptions. Indeed, recent progress in first-principles calculations of optical spectra illustrates that optical and magneto-optical (MO) spectra are developing into a powerful tool for tracing the electronic structure of actinide compounds. Both spectra depend quite sensitively on the underlying electronic structure, and can be utilized to assess the degree of localization of the *5f* electrons. The basic supposition is that optical and MO spectra calculated with itinerant and localized

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electron models are sufficiently different and accurate that comparison with experimental spectra allows a meaningful assessment of the localization.

There are quite a few first-principles calculations of the MO spectra of uranium compounds [3–8]. The MO spectra of such compounds as UAsSe [5] and U_3P_4 [6,8] are well described in the LSDA, and we can conclude that they have at least partially itinerant electron behavior. On the other hand, the MO spectra in US, USe, and UTe can be well described only in the LSDA+ U approximation [7], supporting the localized description for their $5f$ electrons.

In our previous paper we reported the theoretically calculated MO spectra of $UCuP_2$ [9]. Within a band-like description of the $5f$ electrons, good agreement with the measured MO spectra was obtained. In this work we present a detailed theoretical investigation of the electronic structure and MO Kerr properties of the $UCuAs_2$ compound. The nearest-neighbor distance between uranium atoms is increased from 3.80 Å in $UCuP_2$ to 3.95 Å in $UCuAs_2$, and one would therefore expect an increase of the $5f$ localization in going from $UCuP_2$ to $UCuAs_2$.

Experimental measurements of MO spectra in $UCuAs_2$ have been reported by Schoenes et al. in Ref. 10. It was found that the MO Kerr rotation in the ferromagnetic phase reaches a value as high as 1.75° at 1.2 eV. The Kerr ellipticity of $UCuAs_2$ has a maximum value of 1.1° at 2.3 eV [10].

This paper is organized as follows. The computational details are given in Sec. 2. Section 3 presents the theoretical electronic structure and MO spectra of $UCuAs_2$. The results are then compared to the experimental data. Finally, the results are summarized in Sec. 4.

2. Crystal structure and computational details

$UCuAs_2$ belongs to tetragonal As–Cu–Si–Zr crystal structure with the space group $P4/nmm$ (No. 129) with U at the $2c$ position, Cu at the $2b$ position, and As at the $2a$ and $2c$ positions. The lattice constants are $a = 3.951$ Å, $c = 9.558$ Å [11]. The unit cell of $UCuAs_2$ contains 8 atoms.

The details of the computational method are described in our previous paper [9], and here we only mention several aspects. Self-consistent energy band-structure calculations of $UCuAs_2$ were performed by means of the fully relativistic, spin-polarized linear-muffin-tin-orbital (SPR LMTO) method using the atomic sphere approximation with combined corrections included [12–16]. The LSDA part of the energy band-structure calculations was based on the spin-density-functional theory with von Barth–Hedin parameterization [17] of the exchange-correlation poten-

tial. The \mathbf{k} -space integrations were performed with the improved tetrahedron method [18] and charge self-consistently was obtained with 270 irreducible \mathbf{k} points. The basis consisted of U s, p, d, f and g ; Cu s, p, d and f ; As s, p and d LMTOs. We mention, lastly, that the Kramers–Kronig transformation was used to calculate the dispersive parts of the optical conductivity from the absorptive parts.

The application of standard LSDA methods to f -shell systems meets with problems in most cases because of the correlated nature of the f electrons. To account better for the on-site f -electron correlations, we have adopted as a suitable model Hamiltonian that of the LSDA+ U approach [19]. The main idea is the same as in the Anderson impurity model [20]: the separate treatment of localized f electrons for which the Coulomb f – f interaction is taken into account by a Hubbard-type term in the Hamiltonian $\frac{1}{2}U \sum n_i n_j$ (n_i are f -orbital occupancies), and delocalized s, p, d electrons for which the local density approximation is regarded as sufficient.

Let us consider the f ion as an open system with a fluctuating number of f electrons. The formula for the Coulomb energy of f – f interactions as a function of the number of f electrons N given by the LSDA is $E = UN(N - 1)/2$. If we subtract this expression from the LSDA total energy functional, add a Hubbard-like term and take into account the exchange interaction, we obtain the following functional [19]:

$$E = E_{LSDA} + \frac{1}{2}U \sum_{m, m', \sigma} n_{m\sigma} n_{m'-\sigma} + \frac{1}{2}(U - J) \sum_{m \neq m', m', \sigma} n_{m\sigma} n_{m'\sigma} - \text{d. c.}, \quad (1)$$

where

$$\text{d. c.} = U \frac{N(N - 1)}{2} - \frac{JN^\uparrow(N^\uparrow - 1)}{2} - \frac{JN^\downarrow(N^\downarrow - 1)}{2},$$

N is the total number of localized f electrons, N^\uparrow and N^\downarrow are the number of f electrons with spin up and spin down, respectively, U is the screened Coulomb parameter, and J is the exchange parameter.

The orbital energies ε_i are derivatives of (1) with respect to the orbital occupations n_i :

$$\begin{aligned} \varepsilon_i &= \frac{\partial E}{\partial n_i} = E_{LSDA} + (U - J) \left(\frac{1}{2} - n_i \right) = \\ &= E_{LSDA} + U_{\text{eff}} \left(\frac{1}{2} - n_i \right). \end{aligned} \quad (2)$$

This simple formula gives the shift of the LSDA orbital energy $-U_{\text{eff}}/2$ for occupied f orbitals ($n_i = 1$) and $+U_{\text{eff}}/2$ for unoccupied f orbitals ($n_i = 0$). A si-

milar formula is found for the orbital dependent potential $V_i(\mathbf{r}) = \delta E / \delta n_i(\mathbf{r})$, where the variation is taken not on the total charge density $\rho(\mathbf{r})$ but on the charge density of a particular i th orbital $n_i(\mathbf{r})$:

$$V_i(\mathbf{r}) = V_{\text{LSDA}}(\mathbf{r}) + U_{\text{eff}} \left(\frac{1}{2} - n_i \right). \quad (3)$$

The advantage of the LSDA+ U method is the ability to treat *simultaneously* delocalized conduction band electrons and localized f electrons in the same computational scheme. With regard to these electronic structure calculations, we mention that the present approach is still essentially a single-particle description, even though intra-atomic f Coulomb correlations are explicitly taken into account.

3. Results and discussion

The uranium pnictide ternary compounds with copper or nickel crystallize in a high-symmetry structure: UCuP_2 , UCuAs_2 , UNiAs_2 are tetragonal [21] and UCu_2P_2 and UCu_2As_2 are hexagonal [22]. The U–Cu ternaries order ferromagnetically, in contrast to the U–Ni ternaries, which are all antiferromagnets [23]. The magnetic ordering temperatures are among the highest known so far for uranium compounds, reaching 216 K for UCu_2P_2 [24]. The magnetic and transport properties of UCuAs_2 were investigated by Kaszowski et al. [25] on single-crystal specimens. They found that the compound is a ferromagnet below 131 K with a spontaneous magnetic moment of $1.27\mu_B$ per U atom, and in the magnetically ordered region it exhibits large magnetocrystalline anisotropy constants. The electrical resistivity of UCuAs_2 at low temperature behaves as T^2 , while in the temperature range above T_C the observed negative slope of $\rho(T)$ may point to Kondo lattice behavior [25].

The energy dependence of the Kerr rotation and ellipticity of UCuAs_2 have been measured by Schoenes et al. [10]. The measurements were made on a natural grown surface perpendicular to the c axis in the energy range 0.55 to 5 eV and at temperatures down to 2 K in an external magnetic field up to 10 T. Although UCuAs_2 has lower uranium concentration in comparison with the UX and U_3X_4 ($\text{X} = \text{P}, \text{As}$) compounds, its Kerr rotation reaches 1.75° (Ref. 10), which is the largest among these compounds.

The fully relativistic spin-polarized total and partial density of states (DOS) of ferromagnetic UCuAs_2 calculated in the LSDA approximation is shown in Fig. 1. The energy bands in the lowest region between -13.6 and -7.5 eV have mostly As s character, with some amount of U and Cu spd character mixed in. The energy bands between -7.5 and -1.0 eV are As $4p$

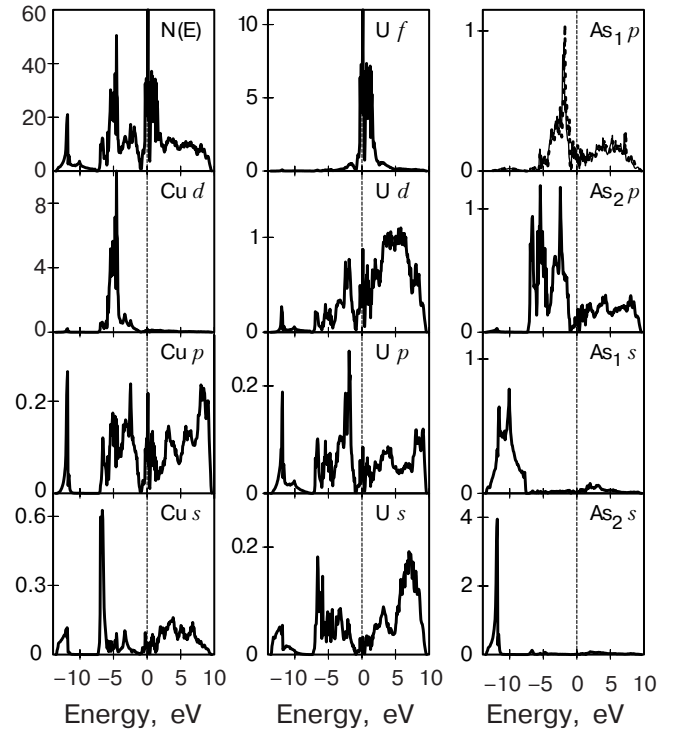


Fig. 1. Fully relativistic, spin-polarized total (in states/(unit cell·eV)) and partial densities of state (in states/(atom·eV)) calculated for UCuAs_2 in the LSDA approximation.

states strongly hybridized with the Cu $3d$ and U $6d$ states. There is a small energy gap between As s and p states. The Cu $3d$ states are fully occupied and situated around 5.0 eV below the Fermi level. The highest region above the Fermi energy can be characterized by antibonding U $6d$ states. The U $5f$ energy bands in LSDA are located above and below E_F at about -0.5 to 1.5 eV. It is interesting to note that the $4p$ partial density of states for As₁ and As₂ sites differ from each other significantly. It reflects the different geometrical positions of the two arsenic atoms. The plane with As₁ atoms is situated between uranium planes, whereas the plane with As₂ atoms is between uranium and copper planes. The As₁ atoms have as neighbors four As₁ atoms at 2.794 Å distance and four uranium atoms at 2.981 Å. On the other hand, As₂ atoms have four Cu neighbor atoms at 2.513 Å distance and four uranium atoms at 2.965 Å. As a result, the $4p$ partial density of states for As₁ site has one peak structure for occupied states reflecting strong hybridization between As₁ $3p$ and U $6d$ states, whereas $4p$ partial density of states for the As₂ site has two additional peaks at -6.5 to 5 eV due to the hybridization of As₂ $3p$ states with Cu $3d$ states.

In our LSDA+ U band structure calculations we started the fully consistent iterations from a $5f^2$ configuration for the U^{4+} ion with two on-site $5f$ levels

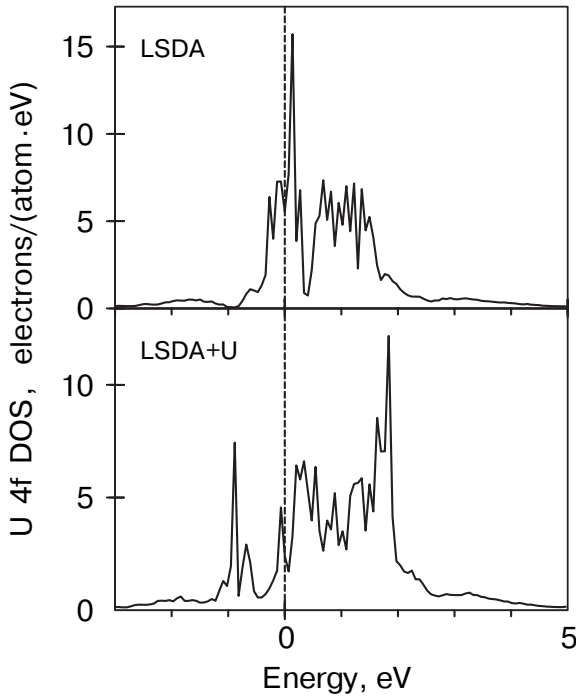


Fig. 2. Fully relativistic, spin-polarized U partial 5f densities of states calculated for UCuAs₂ in the LSDA and LSDA+U approximation.

shifted downward by $U_{\text{eff}}/2$ and twelve levels shifted upwards by this amount. The energies of occupied and unoccupied 5f levels are separated by approximately U_{eff} . The Coulomb repulsion U_{eff} strongly influences the U 5f electronic states in UCuAs₂. The U 5f partial density of states calculated in the LSDA and LSDA+U approximations are presented in Fig. 2.

After consideration of the above band structure properties we turn to the MO spectra. In Fig. 3 we show the calculated and experimental [10] MO Kerr rotation and ellipticity spectra of the UCuAs₂ compound. Better agreement between the calculated and the experimentally measured MO Kerr spectra was found when we used the LSDA+U approximation. The prominent peak at 1.2 eV in the Kerr rotation spectrum originates mostly from U 5f → 6d interband transitions. The interband transitions from Cu 3d to U 5f bands start above 4 eV. The LSDA calculations produce a two-peak structure with the largest peak situated at 0.9 eV. The Coulomb repulsion U_{eff} shifts the energies of occupied 5f levels downwards and unoccupied ones upwards (Fig. 2); as a result, the LSDA+U calculations correctly produce the shape and energy position of the prominent peak in both the Kerr rotation and ellipticity spectra (Fig. 3). On the other hand, the theory, both in the LSDA and LSDA+U approximations, produces a blue energy shift by about 1 eV in the position of the local minimum and second

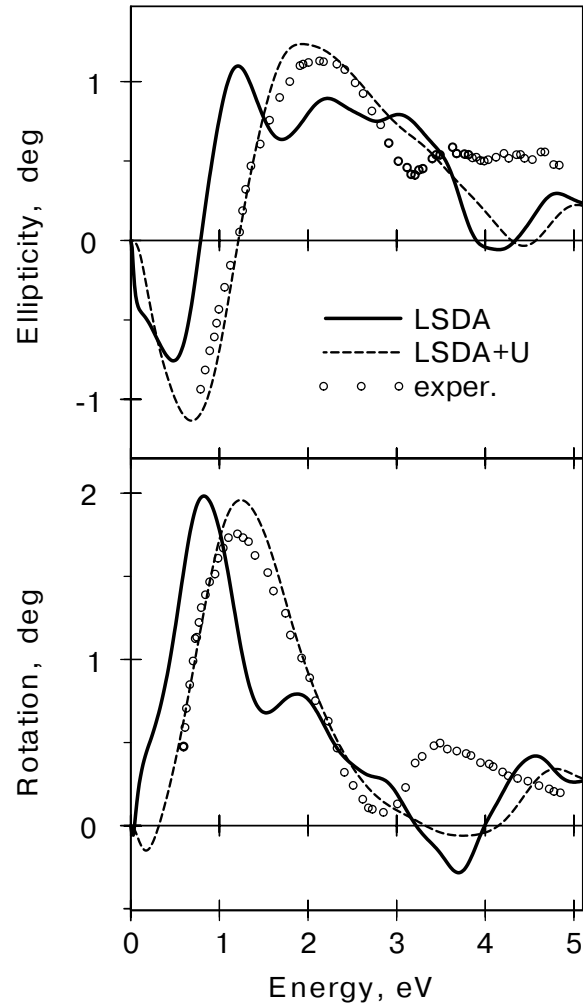


Fig. 3. Calculated and experimental Kerr ellipticity (ϵ_K) and Kerr rotation (θ_K) spectra of UCuAs₂. The experimental data are those of Ref. 10.

high-energy peak in the Kerr rotation and ellipticity spectra in comparison with the experiment.

Table presents a comparison between calculated and experimental magnetic moments in UCuAs₂. The LSDA total magnetic moment on uranium in UCuAs₂ is only 0.641 μ_B (Table) (with spin moment $-1.677 \mu_B$ and orbital moment 2.318 μ_B), which is considerably smaller than the experimental moment of about 1.27 μ_B [10]. The calculated moment is dominated by 5f states: the 5f components of the spin and orbital moment are $-1.569 \mu_B$ and 2.283 μ_B , respectively. It is a well-known fact, however, that within the LSDA the total magnetic moment of uranium compounds in general comes out too small [26–30]. Corrections which simulate Hund’s second rule interactions in solids, describing orbital correlations absent in the homogeneous electron gas, such as the orbital polarization, are needed to bring the magnetic moment into better agreement with experiment [27–30]. On the

The experimental and LSDA calculated spin, orbital and total magnetic moments (in μ_B) of UCuAs₂. The experimental datum is from Ref. 10

Atom	LSDA			LSDA + U			Experiment
	M_s	M_l	M_{total}	M_s	M_l	M_{total}	
U	-1.677	2.318	0.641	-2.135	4.123	1.988	1.27
Cu	-0.020	-0.002	-0.022	-0.017	-0.002	-0.019	
As ₁	-0.003	0.002	-0.001	0.003	0.005	0.008	
As ₂	-0.010	-0.018	-0.028	-0.008	-0.016	-0.024	

other hand, our LSDA+U calculations overestimate the total magnetic moment in UCuAs₂ compound (Table). We should mentioned that it is still not clear how to choose the projections m_l of the orbital momentum onto the spin direction if we have more than one occupied state. From total energy calculations we found that the U⁴⁺ ground state corresponds to the projection of the orbital momentum onto the spin direction equal to $m_l = -3$ and -2 in accordance with all three Hund's rules. The value of the magnetic moment and MO spectra depends strongly on the m_l and it may be better to regard the values of the m_l as parameters and try to specify them from comparison of the calculated physical properties with experiment. We performed calculations for every possible combination of the m_l and found that the best agreement between calculated and measured MO spectra can be achieved with $m_l = -3$ and -2 for U⁴⁺ in UCuAs₂ (in accordance with Hund's rules and total energy calculations). These values give the magnetic moments presented in Table. On the other hand, the theoretically calculated magnetic moments are in better agreement with the experiment for $m_l = \pm 2$ (total magnetic moment at the U site equal to $1.029 \mu_B$ with spin and orbital magnetic moments equal to -1.144 and $2.173 \mu_B$, respectively). Evaluation of the correct magnetic moment in this compound needs further theoretical investigation.

4. Summary

The spectral behavior of the MO Kerr spectra in UCuAs₂ is better described by LSDA+U band-structure theory than by LSDA. This fact indicates that the U 5f electrons in the ternary UCuAs₂ are likely to be partly localized, in contrast to UCuP₂, where the U 5f electrons are itinerant [19]. This supports the conclusion drawn early by Schoenes et al. [10] that the

localization of the f states is increased in going from UCuP₂ to UCuAs₂.

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