High Eu 4f low-energy oscillator strength in the isostructural rare-earth Zintl compounds EuIn_2X_2 ($\text{X}=\text{P}, \text{As}$)

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High Eu 4f low-energy oscillator strength in the isostructural rare-earth Zintl compounds EuIn_2X_2 ($\text{X} = \text{P, As}$)

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The isostructural Zintl compounds EuIn_2X_2 ($\text{X} = \text{P, As}$) are investigated within density functional theory. We employ the local spin density approximation with onsite interaction (LSDA + U) for varying U from 0 eV to 7 eV to model the Coulomb repulsion of the Eu 4f electrons. The LSDA + U optical conductivity disagrees with the experimental spectrum, while the simple LSDA is successful. Contrary to the expectation, it is found that EuIn_2X_2 ($\text{X} = \text{P, As}$) has a large oscillator strength for the $f \rightarrow d$ transitions in the low-energy range (below 1.5 eV) in which effects of the joint density of states play a key role. The materials show a sizeable magneto-optical Kerr effect.

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Since the first presentation of the Zintl concept (formation of compensated valence intermetallic compounds based on a complete charge transfer from an alkali or alkaline-earth element to a post-transition element) by Zintl in the early 1930's, Zintl phases have received great interest because of their fascinating structural variety and wide field of materials applications.¹ Their physical properties include complex magnetic ordering, superconductivity, and colossal magnetoresistance.^{2–4} Among the Eu-containing Zintl compounds, $\text{Eu}_{14}\text{MnAs}_{11}$, Eu_3InP_3 , and $\text{Eu}_3\text{In}_2\text{P}_4$ have been studied intensively.^{5–7} Two new compounds of this family, EuIn_2X_2 ($\text{X} = \text{P, As}$), have been discovered recently.^{8,9}

For EuIn_2X_2 ($\text{X} = \text{P, As}$), the zero field resistivity is maximal near the Neel temperature at $T = 24$ K and 17.5 K for EuIn_2P_2 and EuIn_2As_2 , respectively ($T_N = 24$ K and 16 K, respectively). The room temperature resistivity of EuIn_2P_2 is about $10^{-5} \Omega\text{m}$, indicating a semimetallic nature, while the isostructural arsenide EuIn_2As_2 is metallic. The resistivity increases with T in the high-temperature range, but the increase is not linear. The magnetoresistance is maximal for each compound at the temperature corresponding to the zero field resistivity maximum in the largest measured field (5 T). They are negative colossal magnetoresistant (CMR) materials, with maximal magnetoresistances of -298% (EuIn_2P_2) and -143% (EuIn_2As_2).

The maximal magnetoresistance is higher for the phosphide than the arsenide, which is expected from the magnetic coupling strength. For the phosphide, which has shorter Eu-Eu distances than the arsenide, a larger Weiss constant and the higher ordering temperature indicate a higher exchange energy, i.e., the local moments are more tightly coupled in the phosphide. Supportive of this conjecture, the dominant ferromagnetic interaction when the c -axis is perpendicular to the magnetic field is found for EuIn_2P_2 at lower field strengths than for EuIn_2As_2 . Since the spin ordering likely occurs through the conduction electrons, more tightly coupled local spins will have a stronger effect on the delocalized carriers, thus enhancing the magnetoresistance. Metals

typically have a small magnetoresistance of less than 2%.¹⁰ However, EuIn_2As_2 is a metal with localized magnetic moments in addition to its two-dimensional conduction layers. Consequently, the local spin alignment can affect the resistivity (temperature and field dependence) because of magnetic scattering of the charge carriers.

Only recently, Pfuner *et al.*¹¹ have investigated the optical properties of EuIn_2P_2 in a wide spectral range for varying temperature and magnetic field. They have found features common with related CMR compounds: several infrared peaks in the optical conductivity (OC) and a gain of Drude weight for growing magnetic field. The gain was attributed to an enhancement of the itinerant charge carrier concentration. A similar gain was observed in EuB_6 below the ferromagnetic transition temperature and attributed to the spin-dependent splitting of the electronic bands in the ferromagnetic phase.¹² The peak at 600 cm^{-1} (74 meV) was assigned to transitions across the hybridization gap. Interestingly, the authors report on a pronounced peak at 0.6 eV and a weak peak at 1.1 eV, and attribute them to electronic interband transitions mostly involving the Eu 4f and 5d orbitals. However, this is not a straightforward conclusion, because the oscillator strength of the $f \rightarrow d$ transitions is expected to be small in the low-energy range, owing to the localized character of the f and d orbitals.¹³

EuIn_2X_2 ($\text{X} = \text{P, As}$) is of great interest due to the large MR in these compounds. In order to understand the OC obtained experimentally for EuIn_2P_2 , especially the high oscillator strength of the $f \rightarrow d$ transitions below 1.5 eV, we will derive the optical and magneto-optical (MO) properties from the electronic structure. As analysis tools, the band structure (BS) and density of states (DOS) will allow us to explain the optical and Kerr spectra in terms of electronic interband transitions. We have performed spin-polarized full-potential linearized augmented plane-wave (FP-LAPW) calculations using the local spin density approximation (LSDA) and LSDA plus onsite interaction (LSDA + U) approaches, including the spin-orbit coupling.

We employ the WIEN2K package,¹⁴ which gives accurate results for magnetic systems,^{15,16} together with the crystal structures reported in Refs. 8 and 9. The LSDA + U method

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FIG. 1. Crystal structure of EuIn_2X_2 ($\text{X}=\text{P,As}$).

is used for better accounting for the correlations of the 4f electrons in rare-earth compounds. We apply the rotationally invariant LSDA + U method with the double-counting scheme of Anisimov *et al.*¹⁷ and $U_{\text{eff}} = 2$ eV to 7 eV with a step size of 0.5 eV ($J = 1$ eV). A value of $U = 7$ eV gave in previous LSDA + U calculations for another Eu compound the correct energetical position of the Eu 4f bands.¹⁸ The parameterization of von Barth and Hedin¹⁹ is employed. For the Brillouin zone integration, we choose a set of 480 $\mathbf{k}$ -points in the irreducible wedge of the Brillouin zone. The convergence has been checked by a refined mesh which gave no appreciable changes in energies or other properties. A Gaussian broadening of 0.1 eV simulates the effects of finite life-time and experimental resolution. The spin orbit interaction is incorporated via the second variational method.²⁰ This approach has been used successfully for various rare earth compounds.²¹ The spin quantization axis is set along the (001) direction. EuIn_2X_2 ($\text{X}=\text{P,As}$) crystallizes in a hexagonal structure with space group $P63/mmm$ and atomic coordinates Eu (0, 0, 0), In ($2/3$, $1/3$, u), and P/As ($1/3$, $2/3$, v), where $u = 0.17155$, $v = 0.10706$ for P and $u = 0.32729$, $v = 0.39253$ for As, as determined by neutron diffraction (Fig. 1).⁸

We have performed calculations for two directions of the magnetization: the a -axis and the c -axis. We find ferromagnetic ordering energetically favorable and the a -axis to be the easy axis, in agreement with experiment.⁸ The calculated total magnetic moments ($6.99 \mu_B$ and $6.97 \mu_B$ for EuIn_2P_2 and EuIn_2As_2 , respectively) are almost the same

and close to the experimental values. They are also close to the moment of an Eu^{+2} ion, suggesting that the moments are localized. Since the calculated optical and MO properties are found to be close to each other, we subsequently present results only for magnetization along the easy axis.

The majority spin BSs of the compounds are shown in Fig. 2. The minority spin BSs are similar except for the location of the unoccupied Eu 4f states, which lie 7 eV above the Fermi energy (E_F). Both the LSDA and LSDA + U (U values from 2 eV to 7 eV) methods reproduce the metallic ground state. There are two electron pockets at the M-point when the LSDA is employed. The bottom of the electron pockets is 0.13 eV below E_F and the Eu 4f bands are located just below them. The width of this group of bands is about 0.24 eV. Below them there is an energy gap of 0.5 eV. For the LSDA + U method, the occupied Eu 4f bands move down below E_F , and eventually are centered at -2 eV with a much increased width of 1 eV for $U = 7$ eV. The broadening is ascribed to changes in the hybridization. The electron pockets at the M-point are pushed up above E_F to become unoccupied. The top of the valence band at the Γ -point shifts from -0.87 eV upward slightly across E_F , leading to a hole pocket and preventing the formation of an energy gap. Instead, a broad pseudogap of 1 eV is formed, confirming the very low plasma edge observed in OC measurements.¹¹

One may doubt that the LSDA is adequate for modelling EuIn_2X_2 ($\text{X}=\text{P,As}$). However, Mattheiss²² has correctly argued that the crystal field gap arises from the well described metal hybridization and that the valence and conduction states should be well described by the LSDA as their character is essentially the same. The experimental hybridization gap is about 74 meV (600 cm^{-1}), which is more than twenty times larger than the 3.2 meV energy gap obtained from resistivity measurements in the temperature range from 29 K to 60 K.

According to Figs. 2 and 3, we can divide the electronic states of EuIn_2X_2 ($\text{X}=\text{P,As}$) into five groups. Group (1), in the energy range from -12 to -10 eV, is mainly due to the P/As s states with some admixture of In $5s$ states. Energies much below E_F ensure that these bands almost retain an atomic character with small bandwidth. Group (2), from

FIG. 2. Calculated BSs of EuIn_2X_2 ($\text{X}=\text{P,As}$) using LSDA + U .

FIG. 3. Calculated DOS of EuIn_2X_2 ($\text{X} = \text{P}, \text{As}$) using LSDA + U .

–7 eV to –4 eV is due to the occupied In 5s and P/As p states. These bands are almost degenerate and less dispersive in comparison to the conduction bands. Groups (3) and (4), from 4 eV to E_F , show several sharp DOS peaks centered at ~ 2 eV due to the occupied Eu 4f states. Group (5), above E_F , is mainly derived from hybridization between the Eu 5d, In 5s and 5p, and P/As d states.

Since the real part of the diagonal component of the OC tensor is directly related to both the joint DOS and the transition probabilities,²³ we use the calculated BS to analyze the details of the optical and MO spectra. It is obvious that spin-orbit coupling and exchange splitting, which both are captured by our BS calculations, are necessary to yield a nonzero Kerr effect.^{24–26} The absorptive part of the off-diagonal components of the OC tensor is proportional to the absorption rate difference between the left and right circularly polarized (CP) light. Beyond, its sign determines the spin polarization of the states responsible for the interband transitions.²⁷

Figures 4(a) and 4(b) present the real and imaginary parts of the diagonal component σ_{xx} of the OC tensor, respectively, while Figs. 4(c) and 4(d) refer to the real and imaginary parts of the off-diagonal component σ_{xy} , respec-

FIG. 4. Calculated real/imaginary part of the diagonal and off-diagonal elements of the OC tensor, along with the Kerr angle and ellipticity of EuIn_2X_2 ($\text{X} = \text{P}, \text{As}$). The results are obtained by the LSDA + U method.

tively. Figs. 4(e) and 4(f) give the Kerr spectra of EuIn_2X_2 ($\text{X} = \text{P}, \text{As}$). The calculated optical and MO spectra are almost the same for the two compounds. As expected from the formation of the pseudogap, $\text{Re}[\sigma_{xx}]$ is small at low energy, while several features are observed experimentally. There is a plateau in the energy range from 3 eV to 4 eV, whereas $\text{Im}[\sigma_{xx}]$ shows a deep minimum near 3 eV and a plateau above 5 eV. The main difference between the two compounds is that the minimum of $\text{Im}[\sigma_{xx}]$ is located between 2 eV and 2.5 eV for EuIn_2As_2 . $\text{Re}[\sigma_{xy}]$ is small up to 1 eV, similar to $\text{Re}[\sigma_{xx}]$. For the phosphide, the minimum is found at 3.5 eV and the maximum at 4.5 eV. $\text{Im}[\sigma_{xy}]$ shows similar characteristics in the low and high energy ranges, but the maximum at 2.8 eV and the minimum at 3.8 eV. Surprisingly, the magnitude of σ_{xy} is higher in the energy range from 1 eV to 4 eV for EuIn_2As_2 as compared to its isostructural compound.

Note that the states in group (1) do not contribute to the low-energy OC, since they lie well below E_F . Groups (2) and (3) give rise to almost constant contributions of interband transitions with distinct onset energy. At 2.5 eV, there is a slight shoulder in $\text{Re}[\sigma_{xx}]$, which originates from transitions between the almost dispersionless bands around –1.0 eV, group (4), and the states around 1.5 eV. When the photon energy increases, $\text{Re}[\sigma_{xx}]$ displays a broad maximum with three small humps in the energy range from 2.8 eV to 4.0 eV. There are several contributions to this structure, where the lower two humps mainly come from transitions between occupied Eu 4f and unoccupied Eu 5d states.¹² These two humps evolve to peaks at 0.5 eV and 1.2 eV when the simple LSDA is employed, see the discussion of Fig. 5 below. The positive maximum of $\text{Im}[\sigma_{xy}]$ near 2.8 eV suggests that the interband transitions related to left CP light are enhanced in this energy region. On the other hand, near 3.8 eV, $\text{Im}[\sigma_{xy}]$ shows a deep negative minimum, indicating the dominance of interband transitions related to right CP light. $\text{Im}[\sigma_{xy}]$ is negligible when the absorption coefficient for left and right CP light is equal, i.e., in the low and high energy parts of the spectrum.

In Figs. 4(e) and 4(f), we can see that the Kerr rotation and ellipticity are related to each other: when ϵ_K crosses zero a peak appears in θ_K due to the Kramers-Kronig relation.²⁸ It

FIG. 5. Calculated real part of the OC of EuIn_2X_2 ($\text{X} = \text{P}, \text{As}$) using LSDA, along with the experimental data for EuIn_2P_2 .¹¹

is interesting to note that ϵ_K crosses and/or touches zero a number of times, suggesting that the incident linearly polarized light stays linearly polarized at these frequencies. The first MO resonance is found at 1 eV. The Kerr rotation is minimal at 1.2 eV and maximal at 6.5 eV, while the Kerr ellipticity is maximal at 1 eV and minimal at 7.8 eV. For EuIn_2As_2 , both θ_K and ϵ_K are enhanced between 1 eV and 3.5 eV.

The Kerr spectra depend on the diagonal as well as off-diagonal components of the OC tensor.²⁹ We observe that minima in $\text{Re}[\sigma_{xx}]$ give rise to large Kerr angles in the same energy range. On the other hand, $\text{Re}[\sigma_{xx}]$ is directly linked to the optical transitions, i.e., to the details of the electronic structure. This has far reaching consequences for Kerr effect engineering, provided that the electronic structure can be tailored to enhance the $\text{Re}[\sigma_{xx}]$ minima. In spite of similar magnitudes of σ_{xx} (in the whole energy range), the Kerr effect is stronger for the arsenide in the range from 1 eV to 3.5 eV due to an enhanced σ_{xy} .

In Fig. 5, we show $\text{Re}[\sigma_{xx}]$ as obtained by the LSDA and compare it to the experimental spectrum. The latter exhibits a sharp peak at 0.5 eV and a smaller peak at 1.2 eV, which both are not reproduced by LSDA + U calculations with $U = 7$ eV. Our LSDA results show a strong shoulder at 0.4 eV and a sharp peak at 0.85 eV, similar to the experiment. These peaks originate from the $f \rightarrow d$ transitions. They diminish under LSDA + U treatment, as is shown in Fig. 4(a), because the Eu 4*f* bands lie 2 eV below E_F (Fig. 2). These results are rather surprising, as the oscillator strength for the $f \rightarrow d$ transitions in the low energy range is supposed to be small. The large oscillator strength for transitions with photon energies lower than 1.5 eV is ascribed to the position of the occupied Eu 4*f* bands. For $U = 7$ eV, they are found ~ 2 eV below E_F , resulting in strong spectral features in the energy range from 3 eV to 4 eV. In contrast, they are located 1.5 eV below E_F for the simple LSDA. Since the probability of the $f \rightarrow d$ transitions is small, owing to the localized character of the *d* and *f* wave functions, the large oscillator strength must originate from joint DOS effects.

The OC reveals several features from 2 eV to 4 eV, which are due to transitions between the In 4*p* and Eu 5*d* states. The structures from 3 eV to 6 eV belong to transitions from groups (2) and (3) to group (5). They are insensitive to the inclusion of an onsite interaction, since the Hubbard U mainly affects the location of the Eu 4*f* bands. Thus, the energetical locations and characteristics of bands involved in the strong features of the OC are similar for LSDA and LSDA + U , except for those of interband transitions with Eu 4*f* initial states.

By the localized nature, the 4*f* electrons of rare-earth elements are rather insensitive to the local environment. Consequently, it is reasonable to assume that a value of $U = 7$ eV is also applicable to EuIn_2P_2 .¹⁸ However, the LSDA + U with $U = 7$ eV fails to reproduce the experimental OC, which would be easily understood if the occupied Eu 4*f* bands were located below E_F . This possibility together with the large oscillator strength for the $f \rightarrow d$ transitions in the low-energy range calls for an accurate measurement of the Eu 4*f* energy levels in EuIn_2X_2 ($\text{X} = \text{P, As}$) by, for instance, photoemission spectroscopy.

In conclusion, we have presented a first-principles investigation of the Zintl compounds EuIn_2X_2 ($\text{X} = \text{P, As}$) using density functional theory to explain the optical and MO behavior in terms of the electronic states. At high energy, $\text{Re}[\sigma_{xx}]$ is not sensitive to inclusion of an onsite electron-electron interaction in terms of a Hubbard U parameter, because this would affect mainly the energetical position of the Eu 4*f* states. Occupied Eu 4*f* states are found just below the electron pockets at the M-point. The LSDA + U approach is not suitable for the studied compounds, while LSDA results of the OC show a strong shoulder at 0.4 eV and a sharp peak at 0.85 eV, due to the $f \rightarrow d$ transitions. Virtually, the same OC is obtained by calculations based on the generalized gradient approximation.

The large oscillator strength for transitions with photon energies below 1.5 eV is surprising as the probability of $f \rightarrow d$ transitions is small, owing to the localized character of the *f* and *d* wave functions. It is concluded that the large oscillator strength must originate from a high joint DOS, awaiting experimental verification. We have investigated the origin of the main features of the Kerr spectra and the role of the minima in $\text{Re}[\sigma_{xx}]$. In the low energy range, the Kerr spectra are very sensitive to the shape of $\text{Re}[\sigma_{xx}]$. It would be highly desirable to enhance the minima of $\text{Re}[\sigma_{xx}]$ by, for instance, alloying, pressure, or strain fields.

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