# Empty $4f^1$-State Magneto-Optical Spectroscopy in LaSe

R. Pittini,[1,*] J. Schoenes,[2] F. Hulliger,[1] and P. Wachter[1]
[1]*Laboratorium für Festkörperphysik, Eidgenössische Technische Hochschule, Hönggerberg, 8093 Zürich, Switzerland*
[2]*Institut für Halbleiterphysik und Optik, Technische Universität Braunschweig, Mendelssohnstr. 3, 38106 Braunschweig, Germany*
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We report the first observation of the magneto-optical signal of an empty spin-polarized $4f$ state in a paramagnetic metal. At 1.5 K and in a magnetic field of 10 T the Kerr rotation spectrum of LaSe shows a remarkably sharp *positive* peak of 2.1° at 2.77 eV and a broader and smaller structure at 3.01 eV. A comparison with CeSe, which displays a similar sharp peak with opposite sign but no second peak, gives evidence that the LaSe signal is due to $5d \rightarrow 4f$ $(J = 5/2)$ and $5d \rightarrow 4f$ $(J = 7/2)$ transitions, while the magneto-optical signal in CeSe corresponds to a $4f$ $(J = 5/2) \rightarrow 5d$ transition. [S0031-9007(96)02217-X]

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Magneto-optics is a well established technique for the study of the occupied $f$ states in rare-earth and actinide compounds [1,2]. In most of these materials, the strongest magneto-optical signal arises from $f \rightarrow d$ transitions from occupied $f$ states to empty conduction-band $d$ states. The initial state of the magneto-optical $f \rightarrow d$ transition is usually the $f$ ground state, which also determines the magnetization of the sample. In these materials, the integrated magneto-optical signal of the $f \rightarrow d$ transitions is proportional to the $f$ spin polarization and therefore to the sample magnetization. In general, however, the magneto-optical signal is proportional to the joint spin polarization [3]

$$\langle \sigma_j \rangle = \frac{\sigma_a + \sigma_b}{1 + \sigma_a \sigma_b}, \tag{1}$$

where $\sigma_a$ and $\sigma_b$ are the spin polarizations of the initial state $a$ and the final state $b$, respectively, i.e., [4]

$$\sigma_k = \frac{n_{k\uparrow} - n_{k\downarrow}}{n_{k\uparrow} + n_{k\downarrow}}, \qquad (k = a, b). \tag{2}$$

Here $n_k$ is the number of occupied initial states or empty final states. If one state is fully spin polarized, i.e., in the case $\sigma_k = 1$, the joint spin polarization $\langle \sigma_j \rangle = 1$. If one of the two states is not spin polarized (for example the initial state $\sigma_a = 0$), the joint spin polarization $\langle \sigma_j \rangle$ is equal to the spin polarization of the other state (in the example, the final state $\sigma_b$). Therefore, even a nonmagnetic or a weakly magnetic material, i.e., one with no occupied spin-polarized states, can have a strong magneto-optical signal, if it has *empty* spin-polarized states that can be occupied in the optical absorption process. Materials particularly suited for such a study are lanthanum compounds with occupied $5d$ states. In this case dipole allowed transitions between $5d$ and $4f$ states are to be expected and if the empty $4f^1$ state is spin-polarized by an applied magnetic field of sufficient strength this may open the way to magneto-optical spectroscopy of empty states. In this work, we present measurement of the magneto-optical polar Kerr effect of LaSe and demonstrate for the first time the possibility to study the empty $4f^1$ state by magneto-optical spectroscopy. Evidence that we observe indeed a $5d^1 \rightarrow 4f^1$ transition is provided by a comparison with similar measurements for CeSe [5]. This compound has the same electronic configuration as LaSe, except for the $4f^1$ state which is occupied in CeSe and which makes this compound to order antiferromagnetically below 5.1 K, whereas LaSe is a Pauli paramagnet [6] with a superconducting transition at 1.02 K [7].

Single crystals of LaSe and CeSe were grown by mineralization at a temperature just below the melting point. The sodium chloride crystal structure and the lattice parameters were checked by an x-ray analysis performed on all the batches. The lattice constants are 6.0663(5) and 5.9924(5) Å for LaSe and CeSe, respectively. The single crystals were cleaved in an inert gas atmosphere to parallelepipeds of typically $2 \times 3 \times 3$ mm$^3$. Sample contact to air was carefully avoided to prevent the samples from oxidization on the surface. Results of the near normal incidence optical reflectivity measurements for LaSe and CeSe [5] are displayed in Fig. 1 for the photon-energy range from 0.03 to 12.4 eV. For both materials, the reflectivity below 2.5 eV increases steeply towards the infrared indicating the metallic character of the compounds. The steeper plasma edge of LaSe reflects a little smaller damping of the conduction electrons in this compound compared to CeSe with an occupied $4f$ state which contributes weakly to the scattering. The broad peak with several fine structures observed above 3 eV in both reflectivity curves arises mainly from $4p$ (Se) $\rightarrow 5d$ (La, Ce) interband transitions. The temperature and field dependencies of the reflectivity have been found to be negligible, except for the infrared side of the free electron contribution, which will not be discussed in detail in this Letter.

To determine the optical conductivity (Fig. 2) by a Kramers-Kronig transformation of the reflectivity, the measured reflectivity spectra of LaSe and CeSe have been extrapolated to $\hbar\omega = 0$ using a Hagen-Rubens fit $R = 1 - 2\sqrt{\nu/\sigma_{\mathrm{DC}}}$, with $\sigma_{\mathrm{DC}}$ values determined from the resistivity measurements (50 and 57 $\mu\Omega$ cm for LaSe and

  

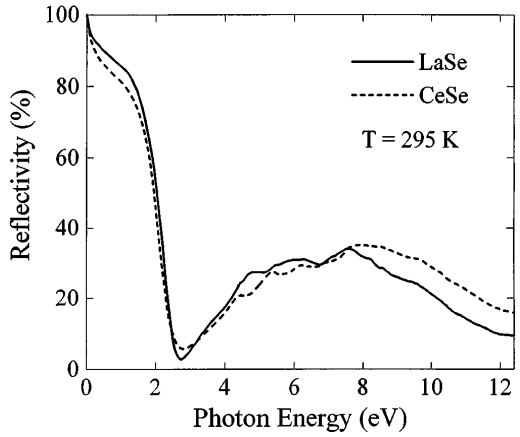


FIG. 1. Optical reflectivity of LaSe and CeSe measured under near-normal incidence in the photon energy range from 0.03 to 12.4 eV.

CeSe, respectively). The UV part of the reflectivity has been extrapolated with a $\omega^{-2}$ law above 12.4 eV and a $\omega^{-4}$ law above 20 eV [8]. The intraband contribution has been determined by fitting the infrared optical conductivity with a single Drude term. The Drude fit yields room-temperature unscreened plasma energies of 4.67 and 4.86 eV for LaSe and CeSe, respectively. Assuming one conduction electron per formula unit, as suggested by a simple ionic model with trivalent La and Ce and divalent Se, effective masses $m^*$ of $1.13m_e$ and $1.09m_e$ are derived from the plasma energies of LaSe and CeSe, respectively. In a quasifree electron model, these values correspond to Fermi energies of 2.21 eV for LaSe and 2.36 eV for CeSe, which are close to the values of 2.41 eV for LaSe [9] and 2.33 eV for CeSe [10] obtained from band structure calculations. The damping $\hbar\gamma$ of the conduction electrons in LaSe was derived from the Drude fit to be 0.27 eV, compared to 0.38 eV in CeSe.

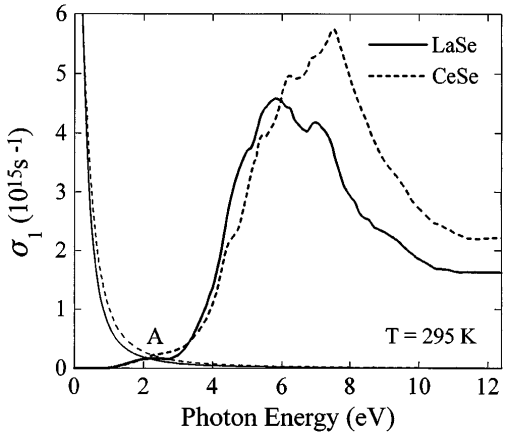


FIG. 2. Real part of the diagonal optical conductivity of LaSe and CeSe. The intraband contribution of the conduction electrons (also shown) has been subtracted to evidence the weak interband transitions near the plasma minimum of the reflectivity.

Weak structures in the spectral region near the plasma edge are clearly resolved between 2 and 3 eV if one subtracts the intraband contribution from the total optical conductivity (Fig. 2). In the remaining interband part of the optical conductivity, most of the structures reflect $4p$ (Se) $\rightarrow$ $5d$ (La, Ce) transitions. The line shapes of the interband optical conductivities of LaSe and CeSe are qualitatively similar.

To measure the low-temperature magneto-optical polar Kerr spectra in the photon energy range 0.55–4.0 eV, an ellipsometer with a Faraday modulator with an accuracy of 0.003° has been used. The measurements have been performed in a magnetic field of 10 T at a temperature of 1.35 K for CeSe and 1.5 K for LaSe. Figure 3 displays the obtained Kerr rotation $\theta_K(\omega)$ and ellipticity $\varepsilon_K(\omega)$ spectra. For CeSe, a sharp negative Kerr rotation peak of $-5.5°$ is observed at 2.6 eV, while in LaSe a sharp positive Kerr rotation peak of 2.1° appears at 2.77 eV, followed by a broader and weaker structure at 3.01 eV. The Kerr rotation observed in LaSe is surprisingly large for a paramagnetic metal. Yet this is not an artifact, since it could be reproduced well in all measured LaSe samples. The main Kerr rotation peaks in LaSe and CeSe correspond to the structure A of the optical conductivity (Fig. 2), i.e., they are associated to the lowest energy interband transition. It is noteworthy that the Kerr rotation peaks are with 0.1 eV remarkably sharp. This points to a transition involving very narrow and highly spin-polarized states, i.e., *f* states. Yet a serious discussion should not be performed on the basis of rotation and ellipticity spectra, but rather on the basis of the off-diagonal elements of the conductivity or the dielectric tensor, since only these quantities separate absorptive and dispersive parts [11].

Figure 4 displays the real and imaginary parts of the complex off-diagonal conductivity tensor element for LaSe and CeSe as computed with the conventional method [1] from the spectra of the Kerr effect and the diagonal conductivity. For CeSe (Fig. 4, right side) one observes at 2.6 eV a single transition with diamagnetic line shape (dispersive

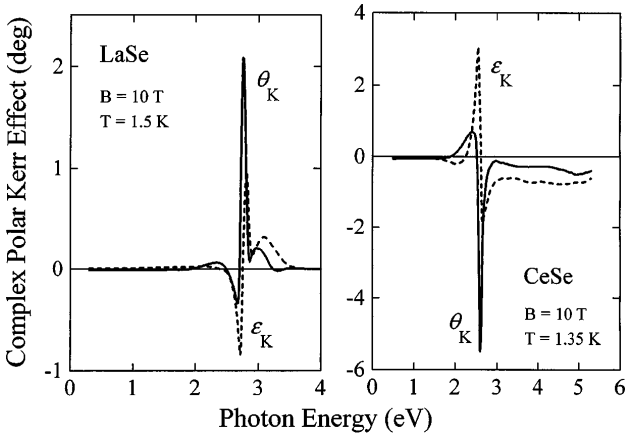


FIG. 3. Measured magneto-optical polar Kerr effect of LaSe and CeSe.

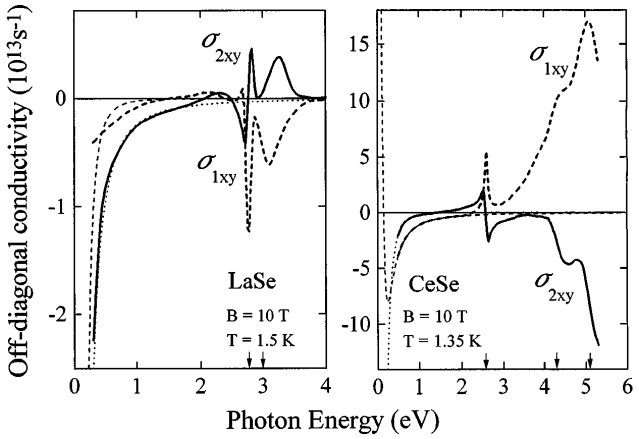


FIG. 4. Experimental off-diagonal conductivity of LaSe and CeSe and fit of the intraband contributions.

line shape in the absorptive part of the off-diagonal conductivity $\sigma_{2xy}$ spectrum, and absorptive line shape in the dispersive part $\sigma_{1xy}$) which has been assigned to a $4f \rightarrow 5d$ transition [5]. Other strongly magneto-optically active absorptions are resolved at 4.3 and 5.1 eV. They have the same line shape as the $4f \rightarrow 5d$ transition centered at 2.6 eV and, therefore, originate from transitions $4f \rightarrow 5d$ [12] to higher-energy final $5d$ states. Correspondingly, the $5d$ density of states obtained from a band structure calculation [10] shows two peaks splitted by 0.9 eV in the region of $5d$ ($e_g$). In the $\sigma_{xy}(\omega)$ spectra of LaSe (Fig. 4, left side) two structures with diamagnetic line shape occur near 3 eV and both have opposite sign compared to the single line in CeSe. Four important conclusions can be drawn from these spectra:

(i) The transformation of the two rotation peaks into two $\sigma_{xy}$ peaks at the same photon energy in LaSe indicates that the dominant Kerr rotation peak, though enhanced by the low values of the optical constants in the vicinity of the plasma minimum of the reflectivity, is definitely due to interband transitions and not simply due to a splitting of the plasma edge in the magnetic field as was first discovered in TmS and TmSe [13].

(ii) The different signs of the lines observed in the off-diagonal conductivities of CeSe and LaSe are understood as follows: The absorptive part of the off-diagonal optical conductivity is given by [3]

$$\sigma_{2xy} = \frac{\pi e^2}{4\hbar\omega}\,\frac{1}{V}\sum_{s,s'}[\omega_{s's}^{-2}|M_{s's}^{-}|^2\delta(\omega_{s's}^{-} - \omega) - \omega_{s's}^{+2}|M_{s's}^{+}|^2\delta(\omega_{s's}^{+} - \omega)], \tag{3}$$

where $M_{s's}^{\pm} = \langle s'|(x \pm iy)|s\rangle$ are the electrical dipole matrix elements between the initial states $s$ and the final states $s'$, and $\omega_{s's}^{\pm}$ are the absorption energies for the right (rcp) and left (lcp) circular light polarizations. The dispersive part $\sigma_{1xy}$ of the off-diagonal optical conductivity can be determined by a Kramers-Kronig transformation of the absorptive part $\sigma_{2xy}$. A sign change of the off-diagonal optical conductivity occurs when the rcp and lcp absorptions are reversed. This arises from a sign change of the selection rule for $\Delta J$ (determined by the matrix elements), which takes place when the same electronic states are involved in the transitions but in reversed order. Therefore, the different sign of the lines in the magneto-optical Kerr spectrum of LaSe and CeSe is strong evidence that we have measured a $5d \rightarrow 4f^1$ transitions in LaSe.

(iii) The two observed interband transitions in LaSe have diamagnetic line shapes as is evident from the two absorptionlike peaks in $\sigma_{1xy}$. A small overlap of the two transitions shifts the negative extremum of the high-energy peaks to a little higher energy than its actual transition energy. The two transitions are determined by deconvolution to be centered at 2.77 eV and 3.01 eV (arrows in Fig. 4) and their energy difference of 0.24 eV is close to the value of 0.27 eV reported for the difference in ionization energies of the $F_{5/2}$ and $F_{7/2}$ states in trivalent cerium [14]. Therefore we assign the two lines at 2.77 and 3.01 eV to the transitions $5d^1$ $(J = 3/2) \rightarrow 4f^1$ $(J = 5/2)$ and $5d^1$ $(J = 5/2) \rightarrow 4f^1$ $(J = 7/2)$. The energy separation of these two transitions is given by the energy difference of the spin-orbit splittings of the $4f$ and $5d$ states. Comparing then the experimental energy difference of 0.24 eV with the spin-orbit splitting of 0.27 eV of the $4f^1$ state, a spin-orbit splitting of 0.03 eV results for the $5d$ states. This is about a factor two smaller than the atomic value [15], as expected for the averaging and partial quenching of the orbital moment in the $d$-conduction band. In the atomic model, the two $5d \rightarrow 4f$ transitions are expected to have diamagnetic line shapes because the same number of rcp and lcp absorptions exist. Counting the number of the dipole allowed transitions, a $3/2$ times stronger weight is expected for the transition $5d$ $(J = 5/2) \rightarrow 4f$ $(J = 7/2)$. Integrating the imaginary part of the off-diagonal conductivity, the weights of $2.04 \times 10^{27}$ s$^{-2}$ and $3.11 \times 10^{27}$ s$^{-2}$ are obtained for $\langle\sigma_{2xy}\rangle$ of the two interband transitions, which corresponds to a ratio of 1.52, in surprisingly good agreement with the simple atomic model. CeSe displays only a single line. This is understood in the present model because only the $4f^1$ $(J = 5/2)$ state is occupied, thus excluding transitions of the kind $4f$ $(J = 7/2) \rightarrow 5d$ $(J = 5/2)$.

(iv) The lines of the $5d \rightarrow 4f$ and $4f \rightarrow 5d$ transitions in LaSe and CeSe are very sharp in the $\sigma_{xy}$ spectra, while they are much broader in $\sigma_{1xx}(\omega)$. This is not due to a temperature dependence of the relaxation time connected with this absorption (in fact, the feature $A$ in $\sigma_{1xx}(\omega)$ is found to be temperature independent), but it originates from the different signals observed in the diagonal and off-diagonal conductivities. As it can be understood from

Eq. (3), the lcp and rcp absorptions mutually cancel in the off-diagonal conductivity, except when spin-polarized and spin-orbit split states are involved in the transitions. In the diagonal optical conductivity, in contrast, the lcp and rcp absorptions are additive. For the states at the bottom of the conduction $5d$ band of LaSe, the $d$-$f$ joint density of states has a van Hove singularity in correspondence with the observed $5d \rightarrow 4f$ transitions. To obtain a strong magneto-optical signal, we reduced the temperature to 1.5 K and applied a magnetic field of 10 T, sufficient to spin-polarize the states at the bottom of the conduction band of LaSe over a width of $2\mu_B B = 1.16$ meV. These are the initial states of the two transitions observed in the off-diagonal conductivity of LaSe, while all the occupied $5d$ states contribute to the peak A in the diagonal conductivity. In CeSe, the initial state of the transition A is a $p$-$f$ mixed state [12]. Its $p$ component does not contribute to the magneto-optical signal in CeSe, since the states of a full valence band cannot be spin-polarized. Therefore, the magneto-optical transition at 2.6 eV is sharp, while the feature $A$ in $\sigma_{1xx}(\omega)$ is broad, as is well reproduced by a recent LDA + $U$ calculation of Oppeneer *et al.* [16].

The energies of 2.77 and 3.01 eV found for the $5d \rightarrow 4f$ transitions in LaSe from our experiment agree well with the theoretical and experimental findings for fcc lanthanum. In fact, in the latter material, the calculated density of empty $4f$ states shows a peak at 2.7 eV [17] and from the peak observed at 5.5 eV in the BIS spectrum, the position of the empty $4f^1$ state is derived to be at 2.6 eV above the Fermi level [18] from an analysis within the framework of a "two electron–one photon transition" assuming a 0.6 eV wide conduction band in fcc lanthanum.

In the last section of this Letter, we like to discuss briefly the free-electron contribution to the off-diagonal conductivity. On the infrared side of the $\sigma_{1xy}(\omega)$ and $\sigma_{2xy}(\omega)$ spectra of LaSe, we observe a negative rise towards $\hbar\omega = 0$. The intraband transitions in LaSe and CeSe have been fitted (Fig. 4) with the conventional method [1,2,5] with a negative spin polarization of the $5d$ states of $-1.6\%$ for LaSe and $-7.2\%$ for CeSe in a field of 10 T at 1.5 and 1.35 K for LaSe and CeSe, respectively.

In conclusion, new measurements of the magneto-optical polar Kerr spectra of LaSe and CeSe demonstrate for the first time that magneto-optics is also a valuable tool for the study of empty $f$ states. We have reported the discovery of a strong magneto-optical Kerr signal in a Pauli paramagnet, showing that the magneto-optical signal is not simply proportional to the sample magnetization, but more generally, it is proportional to the coupled spin polarization of the states involved in the magneto-optical transition. The $5d \rightarrow 4f$ and $4f \rightarrow 5d$ transitions in LaSe and CeSe, respectively, show a dominant line in the Kerr spectrum with the same line shape but opposite sign. LaSe displays an additional line indicating that for the $5d \rightarrow 4f$ transition (in LaSe) both $4f^1$ spin-orbit states $j = 5/2$ and $j = 7/2$ can be optically populated, whereas in the $4f \rightarrow 5d$ transition (in CeSe) only the $4f^1$ ($J = 5/2$) ground state contributes as the initial state. With this result, a new field of research is opened: the magneto-optical study of the empty $f$ states in rare-earth and actinide compounds.

*Present address: Research Institute for Scientific Measurements, Tohoku University, Sendai 980, Japan.

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