PHYSICAL REVIEW B

CONDENSED MATTER

THIRD SERIES, VOLUME 53, NUMBER 16 15 APRIL 1996-II

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Band-theoretical description of the magneto-optical spectra of UAsSe

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(Received 10 October 1995; revised manuscript received 31 January 1996)

The magneto-optical Kerr spectra of the ternary uranium compound UAsSe are investigated using first-principles energy-band theory. Within a bandlike description of the $5f$ electrons, good agreement with the measured optical spectra is obtained. This is further evidence for at least partially itinerant $5f$ electrons in UAsSe, in spite of it frequently being characterized as a localized $5f$ electron system. It is suggested that the $5f$ electrons are delocalized in planes perpendicular to the c axis and that the magneto-optical Kerr spectra are extremely anisotropic.

UAsSe crystallizes in the tetragonal PbFCl crystal structure (also called ZrSiS structure, $P4/nmm$ space group) and orders ferromagnetically along the c axis below $T_c \approx 110$ K.[1,2] Magnetic susceptibility measurements[3] and photoemission experiments[4] supplied evidence for localized $5f$ electrons in UAsSe. On the other hand, reflectivity and magneto-optical (MO) spectroscopy revealed a pronounced spectral intensity at small photon energies (<2 eV), which was attributed to a $5f$ band located at the Fermi energy.[5] Also, the specific-heat coefficient $\gamma = 41\ \mathrm{mJ/mol\,K^2}$ indicates a tendency to itinerancy.[6] These apparently contradictory observations show that the behavior of the $5f$ electrons and the related magnetic properties of UAsSe are not yet well understood. A characterization of the 5f electrons in accord with all of these experiments would be one of, in some sense, partially delocalized or partially localized $5f$ states.

The behavior of the $5f$ states in uranium are commonly believed to range from localized to delocalized as, e.g., in the well-investigated uranium rocksalt compounds such as the uranium monochalcogenides, US, USe, and UTe, which are, just like UAsSe, magnetically highly anisotropic ferromagnets but with the easy magnetization axis being the (111) axis.[7] Within this group of isostructural compounds, US is believed to have practically itinerant $5f$ electrons,[8] while UTe is believed to have quasilocalized $5f$ electrons[9]—a view which is substantiated by a specific-heat coefficient γ, which actually drops as the series is traversed.[10]

It has already been shown that first-principles band-structure theory using the local spin-density approximation[11] (LSDA) has failed in giving a satisfactory description of the optical spectra of the uranium monochalcogenides.[12–14] This failure was thought to be due to an insufficient treatment of the $5f$ electron correlations by the LSDA.[12] The calculated

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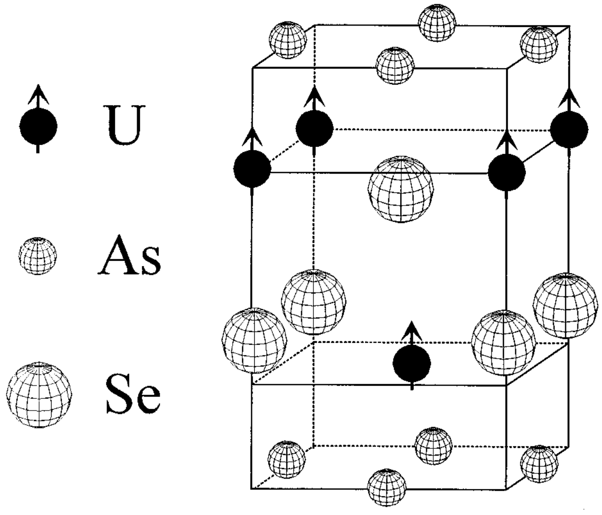

FIG. 1. Crystallographic unit cell of UAsSe in the PbFCl crystal structure. The magnetic moments on the uranium sites are depicted by the arrows.

results[12–14] were worse than those for transition-metal compounds, and also worse than one would expect if the 5f electrons were itinerant. The latter point is especially disturbing, because it might indicate a breakdown of the standard LSDA theory for the excited states in uranium compounds. However, because the measurements on the uranium monochalcogenides were performed in a nonpolar geometry,[15] another explanation could be a geometrical dependence of the Kerr spectra. To investigate separately the effects of geometry and many-body correlations we choose UAsSe for the present study. The MO spectra of UAsSe were measured in the polar geometry,[5] so that we can compare theory and experiment in the best possible circumstances. Also, as in the monochalcogenides[8–10] the 5f electrons in UAsSe are thought to be partially localized.[3,4] Inherent many-electron correlation effects, which can already be important for the proper description of ground-state properties, should become imperative for describing optical excitations, for example, when a strong on-site Coulomb attraction between electron and hole quasiparticles plays a dominating role.[16,17] Therefore, if the uranium 5f electrons are localized, one would particularly expect to observe corresponding correlation effects in the optical spectra.

The unit cell of UAsSe in this structure is shown in Fig. 1. As in other uranium compounds with noncubic structures such as, e.g., the ternary UT_2X_2 compounds,[18] there is the possibility of partially delocalized electrons in another sense. These compounds with a preferred c axis tend to have the uranium atoms arranged in layers, which leads to both anisotropic bonding and magnetic properties due to hybridization of 5f and p or d states. It is quite possible that the 5f electrons are delocalized in the planes but localized along the c axis, and we suspect that this may be the case in UAsSe, which distinguishes it from UAs and USe, both of which are cubic rocksalt compounds.

If the 5f electrons are itinerant in the planes then the Coulomb interaction between electrons in these planes will be well shielded and LSDA should provide an adequate description of charge and current correlations in the planes. There may be, nevertheless, strong electron correlation perpendicular to the planes, and it may well be that LSDA underestimates this correlation and overestimates the shielding of the Coulomb interaction along the c axis. Optical measurements, in which light couples to currents, measure current-current correlations since the optical response is related to these correlations through the fluctuation-dissipation theorem. In UAsSe, the uranium planes are perpendicular to the axis of the reported polar Kerr measurements,[5] so that the polar MO Kerr effect selectively probes these planes, which is a possible explanation[5] of why the response appears to be due to itinerant electrons.

To obtain a better understanding of the behavior of the 5f electrons in UAsSe, we performed first-principles calculations of the energy-band structure, on the basis of density-functional theory in the LSDA.[11] For the description of the LSDA exchange-correlation potential the von Barth–Hedin parametrization was used.[19] The relativistic energy bands were computed using the augmented-spherical-wave band-structure scheme,[20] in which the spin-orbit interaction was included in the second variational step. From the energy-band structure we calculated the optical conductivity spectra, by employing the usual linear-response formalism and a computational technique that we developed previously.[14,21] The MO Kerr spectra can be derived straightforwardly once the complete optical conductivity tensor is calculated,[21] so that a direct comparison between measured and theoretical Kerr spectra can be made. Before comparing these spectra, we mention that the spectra calculated *ab initio* are for the contribution to the optical conductivity from optical transitions between occupied and unoccupied energy bands—the *interband* spectrum. The total optical conductivity and measured spectra contain, in addition, an *intraband* contribution. The intraband contribution is due to various electron scattering processes that may occur at small photon energies.[15] This intraband part of the conductivity may be sample dependent, but it can be reasonably approximated by a Drude-type conductivity.[15]

In Fig. 2 the calculated polar Kerr spectra of UAsSe are shown together with the experimental spectra.[5] Spectral broadening was applied to the calculated spectra by convoluting with a Lorentzian. The amount of broadening is defined by the broadening parameter, which is the half width at half maximum of the Lorentzian. This broadening accounts for finite lifetime effects and experimental resolution.[21] The theoretical Kerr spectra are given for two different broadening parameters, 0.03 Ry (dashed-dotted curve) and 0.04 Ry (solid curve), so that the dependence on the broadening is illustrated. A comparison of the spectra in Fig. 2 illustrates the good agreement between band theory and experiment. Both the position and height of the main peak in the Kerr angle (θ_K) at 3 eV are correct, with the usual (small) dependence of the theoretical peak height on the broadening. There is also a calculated smaller peak in the Kerr rotation at 1 eV, where there is a shoulder in the measured Kerr angle. A Kramers-Kronig related peak structure is visible in the Kerr ellipticity (ε_K) spectrum at 1.5 eV. In this energy region the influence of intraband conductivity may be large enough to make the interband and total spectra differ appreciably. The influence of the intraband contribution may be estimated by adding an intraband Drude-type conductivity to the com-

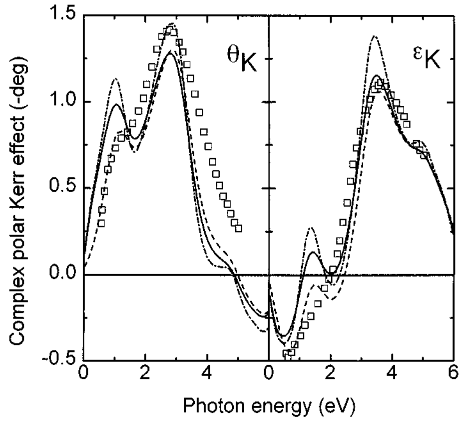

FIG. 2. Theoretical and experimental polar Kerr rotation (θ_K) and Kerr ellipticity (ε_K) spectra of UAsSe. The theoretical, interband-only spectra are given for two different relaxation-time broadening parameters, 0.03 Ry (dashed-dotted curve) and 0.04 Ry (solid curve). The approximate influence of an intraband contribution of Drude form (see text) is illustrated by the dashed curved, for which the interband parts of the spectra are those of the 0.04 Ry relaxation-time broadening. The experimental data (□) are after Reim (Ref. 5).

puted interband conductivity. The resulting calculated Kerr spectra are given by the dashed curve, where the interband conductivity spectra are those for 0.04 Ry spectral broadening, and the parameters of the Drude conductivity are $\sigma_D = 3\times10^{15}$ s^{-1}, $\tau_D^{-1} = 0.02$ Ry. The phenomenological Drude conductivity reduces the height of the peak in the Kerr rotation at 1 eV, but it leaves the peak at 3 eV almost unchanged (see Fig. 2). Also the small maximum in the Kerr ellipticity at 1.5 eV becomes much less pronounced. Thus, although the intraband contribution is only approximate, it definitely brings the calculated Kerr spectra in better agreement with the measured spectra at photon energies below 2 eV.

It is quite surprising—in view of our previous experience with the uranium monochalcogenides[13,14]—that the LSDA band-structure theory gives such a good description of the MO Kerr spectra. If the uranium $5f$ states were localized, then one would expect that the related strong electron correlations would have a substantial effect upon the optical spectra so that these would differ from the LSDA-itinerant electron result.[16,17] This appears not to be the case for UAsSe. We propose that this is because the $5f$ electrons are indeed itinerant in the uranium planes, which are selectively probed by the polar MO spectroscopy. The perpendicular direction is not probed, and with regard to the experiments that support localized behavior,[3,4] it may still be possible that the $5f$ electrons are more localized perpendicular to the planes. If this is the case, then it may even be that $5f$ electron correlation perpendicular to the planes is described poorly by the LSDA, which—due to its construction from the homogeneous electron gas—is a delocalized description in all directions. The LSDA should, nonetheless, reproduce anisotropic bonding and the shielding through the in-plane delocalized electrons better than it describes excited-state properties, which specifically involve electron correlations perpendicular to the planes. We note further that the absolute distinction between localized and delocalized $5f$ electrons is normally a classification stemming from experiment. In comparison to the uranium monochalcogenides, we find that the average extent of the calculated $5f$ wave function in UAsSe is the same as that of USe. The $5f$ states of US are found to be more extended, and those of UTe to be more localized than those of USe.

In spite of the close correspondence between experimental and theoretical Kerr spectra, we find that not all properties of UAsSe are equally well given. The calculated total magnetic moment on uranium is only $0.77\mu_B$ (with spin moment $-1.86\mu_B$ and orbital moment $2.63\mu_B$), which is smaller than the experimental moment of about 1.36–$1.50\mu_B$.[3,22] The calculated moment is practically completely due to the $5f$ states: the f components of the spin and orbital moment are $-1.76\mu_B$ and $2.60\mu_B$, 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.[8,23] Corrections that simulate Hund's second rule in solids, which describes 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.[23] But, for the uranium monochalcogenides a detailed investigation showed that the MO Kerr spectra were almost independent of the orbital moment.[14] It therefore appears that the MO spectra can be properly given by band theory, even if the orbital moment is not. The reason for this is currently being investigated.

The result obtained for UAsSe sheds a new light on the interpretation of the MO spectra of the uranium monochalcogenides. The deviations found previously between the calculated and measured spectra were in the first instance attributed to the occurrence of strong electron correlations,[12–14] which are insufficiently treated within the LSDA. But, in view of the good results obtained for UAsSe, it appears to be unlikely that many-body correlation effects alone are actually responsible for the observed deviations; rather, it is likely that the geometry and orientation of the sample in the

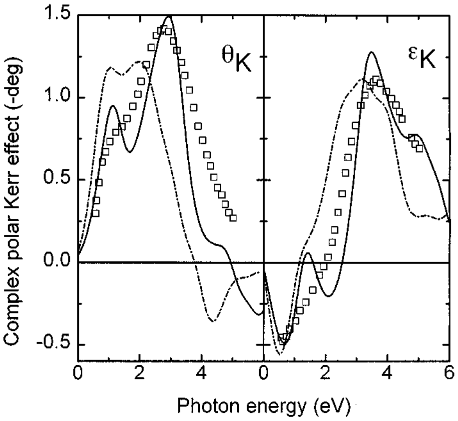

FIG. 3. Geometrical dependence of the calculated polar Kerr spectra of UAsSe. The spectra for which the c axis is the axis of incident light are given by the solid curve, while those for which the a axis is the incident light axis are given by the dashed-dotted curve. In both cases has a Drude conductivity been taken into account and a broadening of 0.03 Ry been applied. Experimental spectra[5] (□) are shown for comparison.

measurements also plays a role. As we mentioned before, the Kerr measurements on the monochalcogenides were performed in a nonpolar geometry.[15] A satisfactory explanation of the MO Kerr spectra of the uranium chalcogenides remains therefore to be found. This, moreover, illustrates that the physics of the uranium monochalcogenides is quite intricate and in many respects still not well understood.

The present result suggests the interesting possibility of measuring the anisotropy of the polar MO spectra in UAsSe or similar compounds. We would expect the MO spectra to be highly anisotropic if the $5f$ states are more itinerant in the planes. For the purpose of comparison with future experiments, we present in Fig. 3 the anisotropic Kerr spectra, which we calculated for the polar Kerr axis (and magnetic moment) oriented along the c axis and along the a axis. The latter geometry probes the MO response of the $5f$ electrons perpendicular to the plane. The intraband Drude conductivity has again been added to the calculated interband conductivities for both orientations. The spectra for the polar a axis differ in the energy range of 1–5 eV substantially from those for the polar c axis, and also from the spectra measured previously.[5] New measurements, in which the polar axis is chosen along the a axis, would therefore contribute valuable information concerning the behavior of the $5f$ electrons perpendicular to the plane.

In summary, we have demonstrated that LSDA band theory can in principle be used for describing the optical spectra of uranium compounds. We furthermore find that the uranium $5f$ states in UAsSe exhibit at least partially itinerant $5f$ electron behavior.

We thank Dr. A. N. Yaresko for calculating the extent of the $5f$ wave functions. This work was supported financially by the State of Saxony under Project No. 4-7541.83-MP2/301. V.N.A. gratefully acknowledges support from the G. Soros Foundation under Contract No. U 42200 (support for Basic Sciences in the former Soviet Union).

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