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Electronic and Spin Structure of UTe

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A self-consistent cellular multiple-scattering technique is used to calculate the density of states of uranium telluride. The $5f$ band is found to be highly polarized and energetically localized although presenting enough itinerant character to keep its position at the Fermi level. The material shows a coupling between the $5f$ and $6d$ states. This interaction explains the observed negative spin polarization from photoelectrons up to 7 eV above the phototreshold.

Negative spin polarization of photoemitted electrons from magnetic materials, i.e., with electron magnetic moments antiparallel to the bulk magnetization and the externally applied field, has been of considerable interest. It was observed in ferromagnetic nickel¹ where it is compatible with both the atomic model of a more-than-half-full shell as well as with the band model in the case of nearly full bands. The occurrence of negative electron spin polarization (ESP) is restricted to within a spectral range of 80 meV from the Fermi level (E_F),¹ which is the order of the smallest Stoner excitation in ferromagnetic nickel. For ferrimagnetic magnetite, Fe_3O_4 , the negative ESP was observed also in a small energy range within E_F . It has been explained by the model of single ion in a crystal field, originating from Fe^{2+} ions in octahedral sublattices which are coupled antiferromagnetically to the rest of the crystal.² Hence, it is a structural property. Recently, the measurements of ESP from ferromagnetic UTe have shown a negative polarization throughout a spectrum of 7 eV below E_F .³ The first attempts to interpret this observation assumed that the $6d$ -electron magnetic moments were antiparallel to the crystal magnetization with the $5f$'s not being observed at low photon energies ($h\nu < 11.0$ eV) due to vanishing matrix elements. Here, we re-

port a theoretical analysis based on a self-consistent cellular multiple-scattering technique. As a major result, it was found that it is not the nature of the $6d$ electronic states alone which are responsible for the observed negative ESP, but the $5f$ resonances located near E_F influencing the $6d$ -electron density of states (d -DOS) in favor of the minority spins and thus creating a trough in the d -DOS of the majorities near phototreshold. By virtue of this f - d interaction, the observed ESP is negative, since, as stated earlier, the $5f$ electrons' contribution to the measured spectra can be taken as negligible.

Usually, the highly localized f -level eigenvalues show a large dependence on occupation. It is necessary to study f -band materials with methods which can treat localized or itinerant levels on equal footing. The method should also be practical for performing a large number of calculations with different assumed configurations in order to find self-consistently the occupation of the different bands. A self-consistent cellular one-electron-Green's-function technique for a finite cluster in condensed-matter-like boundary conditions presents these characteristics.⁴

In the multiple-scattering calculation the local density of states for the atomic species i at energy E is given by the integration over the cell

i of the diagonal elements of the imaginary part of the Green's function so that

$$-(1/\pi) \int_i d^3r \langle \langle \vec{r} | \text{Im} G^+(E) | \vec{r} \rangle \rangle_i = \int \rho_i(\vec{r}; E) d^3r, \quad (1)$$

where $\langle \dots \rangle$ denotes a configuration average with the atom i fixed. The idea of the cluster method is to obtain $\langle \vec{r} | \text{Im} G^+(E) | \vec{r} \rangle$ for a finite cluster in

$$\rho_i(r'; E) = -(1/\pi) \langle \langle \vec{r}' | \text{Im} G^+(E) | \vec{r}' \rangle \rangle_{\text{sph}i} = -(1/\pi) 4\pi \sum_L R_L^2(r'; E) \text{Im} \tilde{G}_{L,i;L,i} \quad (2)$$

where $r' = |\vec{r}'| = |\vec{r} - \vec{r}_i|$, $L = (l, m)$, and $R_L(r'; E)$ are solutions for the radial Schrödinger equation for scatterer i with energy $E = \kappa^2$ and boundary condition $R_L(r'; E) = j_l(\kappa r') \cos \eta_l - n_l(\kappa r') \sin \eta_l$. Here, a (self-consistent) atomic potential $V(r')$ has been used. Furthermore, $\langle \dots \rangle_{\text{sph}i}$ implies angular integration around \vec{r}_i . This radial local density $\rho_i(r'; E)$ can be used to evaluate the atomic quantities shown in (1) or other integrals depending on the local charge density. The calculation of these integrals in terms of angular momentum components are thus straightforward. The potentials are computed from the charge densities using the local exchange $X_{\alpha\beta}$ technique.⁸ A previous application to UN and US showed that in the cubic uranium compounds the Fermi level

the medium under consideration and to average over a collection of such clusters.⁵ For a crystal this average is trivial. An improvement in the representation is obtained with the inclusion of an outside boundary potential for the cluster^{4,6} in a similar manner proposed for molecular multiple-scattering calculations.⁷ The radial local density of states can be written in terms of the angular-momentum-position representation of G^+ as

can be obtained by filling up the levels, including the f band, in an itinerant-electron picture.⁹

The self-consistent potentials $V(r')$ were obtained for UTe with a lattice constant of 11.65 a.u., using an approximation where different potentials for different spins with a final magnetization of $2.16 \mu_B$ per formula unit have been used. The core electrons were computed solving Dirac's equation. The calculation of valence states is nonrelativistic. In the muffin-tin approximation, the sphere radii were 2.835 a.u. for U and 2.451 a.u. for Te. The interstitial potential was

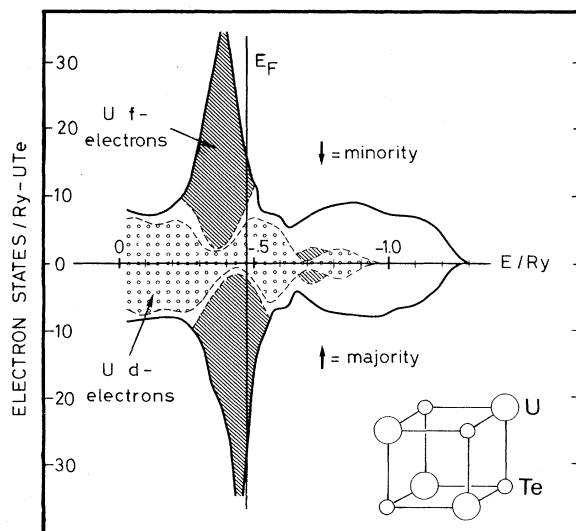


FIG. 1. Local density of states per unit formula and Ry for UTe is plotted as a function of energy in Ry, relative to atomic zero. The hatched and dotted areas represent the f - and d -electron contributions, respectively. The inset shows the arrangement of U and Te atoms in the cluster.

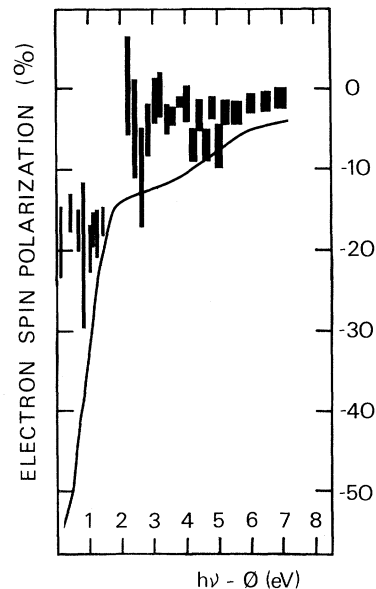


FIG. 2. Theoretical (continuous curve) and experimental (Ref. 3) ESP (in percent) obtained from ferromagnetically ordered UTe. The abscissa for the theoretical curve is electron energy with respect to the Fermi level; the experimental results are plotted as a function of photon energy minus the photothreshold ϕ . The theoretical results include only the s , p , and d electrons.

found to be $V_{\text{int}} = -0.633$ Ry, relative to atomic zero. A cubic cluster of eight atoms (4 U + 4 Te) was used for the calculation (cf. Fig. 1, inset).

In Fig. 1 the DOS for both spins are presented. The hatched and dotted areas represent for each spin the amount of f and d character, respectively. The bands are of a very unique character near E_F but otherwise typical of transition-metal cubic salts.¹⁰ In fact, without the f - d interaction the d bands only show a typical splitting in t_{2g} and e_g parts. The f band induces a further, non-symmetric splitting of the t_{2g} d band with the final result shown. The found spectral exclusion of less localized states coinciding energetically with a narrower band is not new; it is, for example, a known feature in the case of the s - d -hybridization interaction of transition metals.¹¹ An analysis of the cluster orbitals shows that the f - d interaction requires the presence of Te s and p orbitals and, therefore, is more closely described as a superexchange rather than as a hybridization.

As seen in Fig. 1, the s band of Te begins at -1.30 Ry and extends up to above E_F . The p band of Te begins at some higher energy (-1.08 Ry) and extends also beyond E_F for both spins. The amount of f and d character on Te side is very small. On the other hand, the amount of s and p character is small on U side. A uranium conductionlike d band begins at -0.66 Ry, for both spins, but in the valence band the bonding with the Te atoms has U d and f character also at lower energies, as a consequence of the symmetry of the cluster orbitals. The f band has a resonance at -0.37 Ry for the minority spin and at -0.44 Ry for the majority spin, which almost coincides with the Fermi level of the salt.

The spin-orbit interaction, not included in the calculation of the valence and conduction bands, should split the f band by about 1 eV around the shown resonance peaks and introduce some more structure in the DOS, mainly above the E_F . But this splitting is far less relevant to a spin-polarized experiment than the mixing of spin states. To a crude zeroth-order approximation, this will fold a small amount of the spin-up density into the spin-down and vice versa. This will reduce the size of the theoretical curve near zero in Fig. 2 in better agreement with experiment.

Figure 2 shows experimental and theoretical ESP. The measured values are presented as rectangles, according to the uncertainties of the photon energy of excitation and of the polarization measurement. $P(h\nu)$ has a value of -19%

near the photothreshold and remains so within 2 eV below it. At higher energies, $P(h\nu)$ drops to lower values; however, it remains negative up to $h\nu = 11.0$ eV. Note that ESP measures the contribution of all the emitted electrons at a particular photon energy without kinetic-energy discrimination. Therefore, $P(h\nu = 11.0$ eV) contains all s , p , and d electrons. The fact that ESP is always negative rules out the emission of all the $5f$ electrons, which carry the major magnetization. This observation indeed is compatible with the small matrix elements for photoexcitation of f electrons at low photon energies. In the same figure, also shown is a theoretical (integrated) ESP, as a continuous curve, based on the DOS given in the previous figure. In the calculation of ESP only the s , p , and d electrons are included, assuming all having the same oscillator strengths. The amount of d emission at photothreshold, in fact, is lower than that of s and p electrons which could explain the difference between the experimental and theoretical results. The overall features of both ESP are similar. Therefore, this model, albeit simple, provides a very successful qualitative picture in the analysis of the anomalous sign in photo-ESP.

In fact, the occupied part of the d band of U contains more electrons of minority spin than of majority spin, appearing as if it were polarized against the f moment. This is not accidental and we have found similar features in other ferromagnetic uranium salts theoretically and experimentally.¹² For antiferromagnetic cubic salts, e.g., UN, USb, this behavior is only local and the polarization of the d band of uranium averages to zero.

One of the main conclusions drawn from the process of the self-consistent calculation is that the uranium f band is localized enough to resist an increase of occupation over about 2 electrons of the majority spin or the results lead to an inconsistent position relative to the Fermi level. This behavior is strikingly different from that of the rare earths where, when the total energy is minimized, the f -band one-electron eigenvalues can be below E_F and nevertheless only partially filled. In these cases the one-electron eigenvalues cannot be properly identified with the elementary excitations of the system.

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Time-Resolved Photoluminescence Spectroscopy in Amorphous As_2S_3

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Measurements of time-resolved photoluminescence spectra at 2 K from amorphous As_2S_3 on a 10-nsec time scale demonstrate that two independent luminescence processes exist simultaneously. The higher-energy luminescence process at 1.75 eV has a very short lifetime and is rapidly quenched at higher temperatures. The other process appears at lower energy (1.45 eV) and shifts to considerably lower energy with increasing time delay. A model to explain this result is proposed.

Localized states in the gap of amorphous solids are believed to be responsible for many unique properties of these materials. Several models, incorporating Anderson's idea of the negative correlation energy,¹ have been proposed to explain the microscopic origin of these defect states.²⁻⁵ Photoluminescence is a powerful tool for studying these localized states.⁶⁻⁸ We show that investigations of the dynamics of photoluminescence processes provide new insight into the nature of localized states in amorphous solids.

We report the first measurements of the time evolution of the photoluminescence spectra from an amorphous solid (α - As_2S_3) with 10-nsec time resolution. A single, fast luminescence process, occurring at $\frac{2}{3}$ band-gap energy and decaying within the time resolution of 10 nsec, was recently reported by Murayama *et al.*⁹ In contrast to this, our measurements reveal that (1) two in-

dependent luminescence processes occur simultaneously in α - As_2S_3 at short times, (2) these processes are independent of samples, (3) the high-energy process (HEP) decays rapidly in time without any spectral shift and is very strongly temperature dependent, and (4) the spectrum of the low-energy process (LEP) shifts drastically to lower energy with increasing time delay (τ). For $\tau > 200$ nsec, the spectrum becomes similar to the half-band-gap luminescence observed in cw or long-pulse excitation, thus establishing a connection between the short- and long-time processes. We present a model to explain these observations, which cannot be adequately understood by existing models of defect states. Furthermore, the observed properties of the HEP are different from the properties of excitons recently discussed by Street.⁷ In this case, our results indicate that additional states in the forbid-