samples with different Nd^{3+} concentrations in order to establish the concentration dependence of the diffusion parameters, which can then be compared to the variation of the quenching rate. Also, these experiments will be extended to low temperatures to see whether any coherent contribution to the exciton migration can be detected.[20]

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5*f*-Electron Localization in Uranium Compounds

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Observed 7-eV satellites in the x-ray–photoemission spectra of UGa$_2$ and other *B*-group compounds are shown to be due to two-hole final states as confirmed by existing Auger data. The presence of these satellites is an indication for a weak *fd* hybridization and, when compared to uranium–transition-metal compounds, increased 5*f* localization.

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The nature of the 5*f* electrons in the actinides has attracted much attention both from the experimental and the theoretical point of view. For α-U metal it has been shown recently that the 5*f* electrons have primarily itinerant character.[1] The degree of 5*f* localization depends on the overlap of the corresponding 5*f* wave functions on neighboring atoms and on the 5*f*-6*d* hybridization. Since in uranium compounds the interatomic U-U distance and the bonding properties are changed as compared to α-U, a change in the degree of the localization can be expected.

X-ray photoemission spectroscopic (XPS) investigations on uranium compounds with *B*-group elements have shown a characteristic satellite structure at 7 eV higher binding energy of the U 4*f* core-level spectra (see Table I). The only serious attempt to explain these structures has been made for UO$_2$ where this satellite has been attributed to a shakeup process from the oxide-derived *p* band to unoccupied 5*f* states.[2,3]

In this Letter we show that, in the XPS spectra of the intermetallic compound UGa$_2$, a similar structure exists for the U 4*f* as well as for the U 5*f* levels (we note that even the valence bands of UO$_2$ show such a structure, which has been interpreted as belonging to the O 2*p* band[2]). In UGa$_2$ this structure cannot be explained by a shakeup process; thus we conclude that a final-state screening mechanism is responsible for the 7-eV–satellite phenomenon in uranium compounds. On the basis of the Kotani-Toyozawa (KT) model[4] we interpret the satellites as being due to a two-hole final state in the photoemission process and justify this assumption by comparison with existing Auger data. In this way we show, for the first time, that the presence of the 7-eV satellites is an indication for a decreasing *fd* hybridization and consequently increasing $5f$ localization in uranium compounds.

The XPS measurements were performed with a VG-ESCA-III electron spectrometer. For further details concerning measurement and sample preparation, see Schneider and Laubschat.[5] The U $4f$ core-level spectra of UGa_2 were excited by Mg $K\alpha$ x rays, in order to avoid an overlap with a strong Ga Auger line in the Al $K\alpha$ excited spectrum. In the light of the KT model we analyzed the data with a combination of a Doniach-Sunjić (DS)[6] line shape and a Lorentzian convoluted with the spectrometer resolution function.[5] An integral background due to inelastic scattering of the electrons on their way through the sample was accounted for and the Al $K\alpha_{3,4}$ and Mg $K\alpha_{3,4}$ x-ray satellites were subtracted in a first step of the analysis.

The valence band and the U $4f$ core-level spectra of UGa_2 are shown in Fig. 1. The full curve represents the result of a least-squares fitting procedure. The energy separation between the main lines and their respective satellites is determined to be 7.0 ±0.1 eV. The other fit parameters are discussed elsewhere.[7] Another weak structure is observed at about 16 eV higher binding energies in the U $4f$ core-level spectra, which may be due to a U-$6p_{3/2}$–U-$5f$ shakeup process. This structure will not be discussed further.

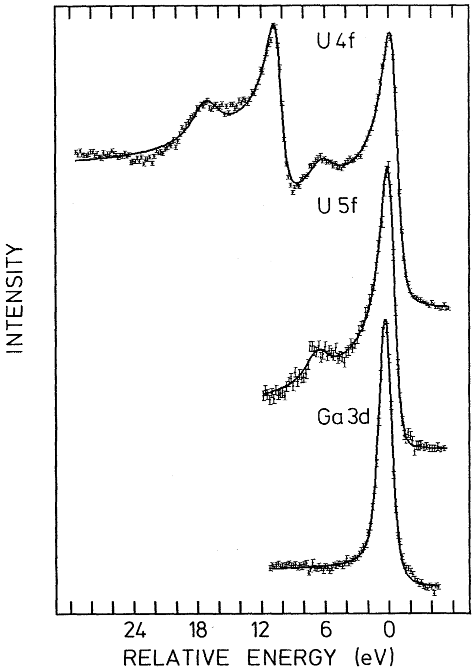

FIG. 1. XPS spectra of the U $4f$, U $5f$, and Ga $3d$ region in UGa_2 excited with Mg $K\alpha$ and Al $K\alpha$ radiation, respectively, drawn on a relative energy scale. The $K\alpha_{3,4}$ satellites have been removed numerically. The binding energies relative to E_F are for U $4f_{7/2}$, 377.5 ± 0.1 eV; for U $4f_{5/2}$, 388.4 ± 0.1 eV; and for Ga $3d$, 18.4 ± 0.1 eV. The Fermi level is located at 0.3 eV lower binding energy relative to the $5f$ maximum. The full curve represents the result of a least-squares fit, where the line shape, according to the KT model, consists of a superposition of a DS line with a Lorentzian. The position of the satellite is determined to be at 7.0 ± 0.1 eV relative to the main line.

Let us now consider the possible mechanisms responsible for the 7-eV satellites. Plasmon losses must be excluded because these structures are only observed in connection with uranium levels and not with gallium levels. Valence effects can be ruled out because the chemical shift even for U^{6+} in UO_2F_2 is less than 6 eV,[8] and, furthermore, such a high valency of uranium is very unlikely in intermetallic compounds. Multiplet splitting cannot be responsible either, because the final-state multiplets for the U $5f$ states in UO_2 differ only by about 1 eV,[2] and, furthermore, a multiplet effect should lead to different splittings for the U $4f_{7/2}$ and U $4f_{5/2}$ as well as for the U $5f$ states. Consequently, these satellites are due to many-body effects.

One possibility is a shakeup process which is defined as being due to a transition from an occupied region of high density of states to unoccupied ones. Thus, only $5f$-$5f$ transitions could be expected in UGa_2 because the broad *spd* bands cannot lead to sharp satellites. Sharp $5f$-$5f$ satellites could only be expected if there is a gap near E_F. This is the case in UO_2 where the energy separation between occupied and empty $5f$ states is about 5 eV.[2] This is, however, too small to explain the 7-eV satellite in UO_2.

Thus, only a final-state screening mechanism has to be considered. The equality of the energy separations between the U $5f$ and the U $4f$ satellites relative to the main lines in UGa_2 indicates a similar screening process for the different states. Similar satellites in various uranium compounds should be indicative for the same screening mechanism. Available data are displayed in Table I. There are two interesting features concerning this table: (i) The satellite appears to be dependent on the angular momentum character of the valence band; increasing *d* character suppresses the satellite intensity. (ii) Materials with large interatomic spacing and with the final-state satellite show higher effective paramagnetic moments than materials without a satellite in the XPS spectrum. As the paramagnetic moments are related to the $5f$-electron localization, the satellite seems to be correlated with the *fd* hybridization.

One way to describe a correlation between a screening process and *fd* hybridization is given by the KT model: The potential of the photohole leads to a deformation of the density of states which is formally described by a lowering of an unoccupied localized state. In the case where this level is pulled below the Fermi energy the probability for occupation is determined by the *fds* hybridization in the initial and final states. This leads to energetically distinct final states and therefore to satellite structure in the XPS spectra.

TABLE I. Nearest interatomic U-U spacings, effective paramagnetic moments, and estimated 7-eV XPS satellite intensities for various binary uranium compounds. w = weak.

Material	U-U distance (Å)	$\mu_{\rm eff}$ (μ_B per formula unit)	Satellite intensity (%)
UF_4	4.52	3.3[a]	10[b]
UO_2	3.86	3.2[a]	10[c]
UGa_2	4.01	3.2[a]	10[d]
UAl_2	3.38	2.9[e]	5[f]
UAs	4.08	3.4[a]	5[g]
UPd_3	4.81	2.6[a]	5[h]
UCu_5	4.96	2.3[h]	5[i]
UAu_3			(5)[j]
UPt	3.61	2.6[a]	w[k]
UPt_2	3.81	2.0[a]	w[k]
UPt_3	4.12	2.6[a]	w[k]
UPt_5	5.25	2.7[a]	w[k]
UNi_5	4.80	...[l]	...[i]
α-U	2.75	...	...[m]

[a] Ref. 9.
[b] Ref. 3.
[c] Ref. 2.
[d] This work.
[e] Ref. 10.
[f] Ref. 11.
[g] Ref. 12.
[h] Ref. 13.
[i] Ref. 14.
[j] Ref. 5.
[k] Ref. 7.
[l] Ref. 15.
[m] Ref. 16.

Because of orthogonality, in uranium metal the occupied lowered state can only have $5f$ or $6d$ character. Let us consider an atomic picture with six valence electrons. In the case of, e.g., a $5f$ ionization, this would lead to the following three final-state configurations:

$$5d^{10}5f^{n}(6d7s)^{6-n}+\hbar\omega \to 5d^{10}5f^{n-1}h(6d7s)^{6-n}+e^{-}, \qquad (1)$$

$$5d^{10}5f^{n-1}6d(6d7s)^{6-n}+e^{-}, \qquad (2)$$

or

$$5d^{10}5f^{n-1}5f(6d7s)^{6-n}+e^{-}, \qquad (3)$$

where n may be nonintegral in the solid state and h represents the unoccupied lowered final-state orbital.

In α-U, because of the strong *fds* hybridization, the spectroscopic lines should correspond to the screened final-state configuration (3). Therefore, it is suggested that the main lines in the compounds correspond to the same final-state configuration. Thus the observed satellite must be identical to a poorly screened one-hole or two-hole final state.

If there are two-hole final states in uranium compounds, created by photoionization, a comparison with Auger processes should be possible.[17] Since the XPS main line is considered to be screened by $5f$ electrons, we have to start with a completely screened primary hole, e.g., in the $5d$ orbital of uranium, and consider a super–Coster–Kronig (SCK) Auger process. Thus the SCK process without screening in the final state can be written as

$$5d^{9}5f^{n}5f(6d7s)^{6-n} \to 5d^{10}5f^{n-1}h(6d7s)^{6-n}+e_{\rm Auger}. \qquad (4)$$

The resultant final state is identical to the unscreened XPS final state (1) and may be screened as follows:

$$5d^{10}5f^{n-1}6d(6d7s)^{6-n}. \qquad (5)$$

A final-state $5f$ screening

$$5d^{10}5f^{n-1}5f(6d7s)^{6-n} \qquad (6)$$

is impossible because the corresponding $5f$ screening orbital is occupied in the initial state and, consequently, the screening charge and the Auger electron cannot be generated at the same time in the same state.

The energy of such a *hypothetical* Auger proc-

TABLE II. Comparison of measured Auger energies (Ref. 18) with XPS binding-energy differences (Ref. 16) [see Eq. (7)] for α-U and UO_2. All energy values are quoted with respect to the Fermi energy. The Auger data from Ref. 18 have been corrected by the work function of the spectrometer (5 eV) and are in good agreement with Ref. 19.

	Auger[a]		XPS[b]	
Material	Transition	Energy (eV)	$E(5d) - E(5f)$ (eV)	ΔE (eV)
α-U	$O_4O_{6,7}O_{6,7}$	99.6 ± 1.0	102.8 ± 0.2	3.2 ± 1.0
	$O_5O_{6,7}O_{6,7}$	91.0 ± 1.0	94.2 ± 0.2	3.2 ± 1.0
UO_2	$O_4O_{6,7}O_{6,7}$	95.5 ± 1.0	102.9 ± 0.7	7.4 ± 1.2
	$O_5O_{6,7}O_{6,7}$	86.7 ± 1.0	95.1 ± 0.7	8.4 ± 1.2

[a] Ref. 18.

[b] Ref. 16.

ess (6) is given by

$$\begin{aligned} E_{\text{Auger}} &= E_{\text{initial}} - E_{\text{final}} \\ &= |5d^9 5f^n 5f(6d7s)^{6-n}| \\ &\quad - |5d^{10} 5f^{n-1} 5f(6d7s)^{6-n}| \\ &= E_{\text{XPS}}(5d) - E_{\text{XPS}}(5f) \end{aligned} \qquad (7)$$

and therefore can be calculated with use of XPS data. A comparison of Eqs. (1)–(3) with (4)–(6) shows that the difference in energy between measured Auger lines and values derived from XPS data should agree with the observed XPS satellites [see Eq. (7)]. The corresponding values for α-U and UO_2 are displayed in Table II. We observe different energy differences for α-U and UO_2. We mention that the special choice of the SCK process (4) involving the $5f$ screening orbital yields an upper limit for the Auger energies. Consequently, the differences in the last column of Table II are slightly larger (in the order of the half width of the occupied $5f$ band) than the real energy differences between the final states (4) and (6), and (5) and (6), respectively. Taking into account this correction the energy differences for UO_2 are in excellent agreement with the 7-eV satellite in this compound.

If we consider that in UO_2 the atomic $6d7s$ orbitals of U are strongly hybridized with O $2p$ orbitals, a damping of the screening process (5) can be understood and, therefore, we identify the XPS satellite and the Auger line in UO_2 with the unscreened final states (1) and (4).

The values for the Auger lines in α-U suggest the existence of satellite structures in the XPS spectra at an energy separation of about 3 eV which then could be due to a d screening (5). In intermetallic compounds, unfortunately, these satellites are in the same energy range where possible oxide contamination is expected. However, Iwan, Koch, and Himpsel[19] recently suggested the existence of such a satellite in α-U manifesting itself as a weak shoulder in the U $5f$ spectra. This effect may also contribute to the asymmetry and linewidth of the U $4f$ peaks in, e.g., uranium-platinum compounds.[5] We mention that a corresponding shoulder in the U $4f$ spectra of UO_2 and in the U $5f$ spectra of UGa_2 is not observed. This means a weak d screening in these compounds which is consistent with the Auger data for UO_2 and our satellite interpretation.

In this context it is interesting to note that, in Th metal, such a 3-eV satellite has been observed,[20] whereas in ThO_2,[3] a 7-eV satellite has been detected. These satellites may be described in the same picture as in α-U and UO_2.

In conclusion, we have shown, for the case of UO_2, the existence of unscreened two-hole final states, which lie 7 eV below the completely screened states. As this state can be considered as quasiatomic, this result can be generalized independent of the particular compound. The presence of the 7-eV satellite in the XPS spectra of uranium–B-group compounds is therefore an indication for a weak fd hybridization and—as compared to uranium–transition-metal compounds—an increased $5f$ localization.

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Transient Effects in Chalcogenide Glasses

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Significant field effects have been reported in chalcogenide glasses, despite the pinning of the Fermi energy by valence alternation pairs. It is shown that the existence of a potential barrier between the two neutral defect centers is responsible for this, but the field effect should decay away with time. It is predicted that the relaxation times are temperature activated, and the activation energies can be used to determine the density of localized states in the gap. New experimental data are reported which demonstrate all of these effects.

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Recent progress in understanding the unique properties of chalcogenide glasses was spurred by the suggestion of Anderson[1] that electrons in states near the Fermi energy E_F are characterized by a negative effective correlation energy, U_{eff}. Street and Mott[2] proposed that this negative U_{eff} is associated with electrons localized on well-defined defect centers. Kastner, Adler, and Fritzsche[3] showed how these concepts follow naturally from the electronic structure of chalcogen atoms, and identified the local nature of the resulting charged defect centers. Adler and Yoffa[4] demonstrated how a negative U_{eff} strongly pins E_F even when the charge density is varied, a result which indicates the absence of a significant steady-state field effect, as we now show.

We assume that a single type of valence alternation pair (VAP)[3] has a creation energy sufficiently smaller than that of any other defect so that it is the origin of the vast majority of the localized states in the gap of the chalcogenide glass. The positively charged center then acts like an ionized donor while the negatively charged center acts like an ionized acceptor. We take the zero of energy as that of the ionized donor. Let T_0 be the energy of the neutral donor and T_0+W the energy of the neutral acceptor. (Note that W can be positive or negative, depending on which neutral center has the lower total energy.) But the ionized acceptor must have energy $2T_0-U$, where U is the magnitude of U_{eff}. The average occupation of the states in the gap is then given by[4]

$$\bar{n}=2\{\exp[-(T_0-\mu)/kT]+\exp[-(T_0+W-\mu)/kT]+\exp[-(2T_0-U-2\mu)/kT]\}/Z, \quad (1)$$