Electronic structure and magnetism of $U_x Th_{1-x}Sb$ as studied by photoemission

B. Reihl, N. Mårtensson, and D. E. Eastman IBM T. J. Watson Research Center, Yorktown Heights, New York 10598

O. Vogt

Laboratorium für Festkörperphysik, Eidgenössische Technische Hochschule, 8093 Zürich, Switzerland (Received 30 March 1981)

Using photoelectron spectroscopy with synchrotron radiation in the $10 \le h\nu \le 130$ eV range, we have studied the "5*f*, 6*d*" electron states in single crystal $U_x Th_{1-x}Sb$. We find that uranium has a quasilocalized 5*f* resonant level with essentially a trivalent configuration and does not change valence in the ordered magnetic region $1.0 \ge x \ge 0.3$ while thorium contributes 6*d* conduction-band electrons which play an important role in both the electronic and magnetic properties.

At present, the general belief is that 5f electrons principally determine the electronic and magnetic properties of the entire actinide series and their compounds.^{1,2} While this may be true for the heavier actinides (starting with Pu) which resemble a second rare-earth series due to 5f localization, the 5f electrons are spatially less localized in the lighter actinides $(Z \leq 93)$ such as uranium and interact with 6d conduction electrons. In the case of the uranium monochalcogenides and -pnictides, this has led to the concept of a "5f, 6d" hybridized conduction band³ dominated by a narrow ~ 1.5 -eV-wide resonant 5f state. In the ferromagnetic U chalcogenide UTe, 5fand 6d electrons have been distinguished via spinpolarized photoemission measurements⁴ which show that the 6d electrons are polarized and aligned antiparallel to the predominant 5f moments.

In this paper we report high-resolution photoemission studies of the 5f and 6d electrons in the $U_x Th_{1-x}Sb$ system, which is interesting in that the number of f and d electrons can be varied due to the atomic configurations of $U(5f^36d^17s^2)$ and $Th(6d^26s^2)$. As reported by Cooper *et al.*,⁵ this system exhibits an interesting and complex magnetic behavior, with an ordered moment occurring for U concentrations $x \ge 0.3$ and an antiferromagnetic-toferromagnetic phase transition at $x \cong 0.83$. For this system, we find that uranium maintains a constant valence (trivalent U^{3+}) with 5f electrons that can be described as a quasilocalized $5f^{3-\delta}$ resonant level, while thorium atoms contribute 6d conduction electrons which fill d bands at the Fermi energy E_F .

This 5f resonant level does not stay pinned at E_F , indicating that it cannot be described simply by an itinerant 5f band but involves correlation effects, at least for the excited states probed with photoemission. We conclude that thorium-derived 6d electrons also play an important role in the magnetic properties of $U_x Th_{1-x}Sb$. Namely, a simple model with polarized Th 6*d* electrons aligned antiparallel to the U 5*f* moment is shown to describe the concentrationdependent ordered magnetization for $1.0 \ge x \ge 0.3$. Likewise, it is suggested that Ruderman-Kittel-Kasuya-Yosida (RKKY)-type magnetic interactions of the 5*f* moments and 6*d* conduction electrons might be involved in the complicated magnetic phase transitions exhibited by this system.

Photoemission measurements were made with a display-type analyzer⁶ using synchrotron radiation at the Synchrotron Radiation Center of the University of Wisconsin-Madison. This system was operated in an angle-integrated mode with a full 86° acceptance cone of emission angles and with an energy resolution of ~0.14 eV. Angle-integrated energydistribution curves (EDC's) were measured using single crystals of $U_x Th_{1-x}Sb$ (x = 0.0, 0.34, 0.85, and 1.0) of dimensions $\sim 3 \times 3 \times 5 \text{ mm}^3$ which were cleaved along their (100) planes and studied in situ in a vacuum of better than 1×10^{-10} Torr. Under these conditions, photoemission and Auger spectra showed that samples stayed clean for several hours. Lowenergy-electron-diffraction spectra (LEED) showed regular $p(1 \times 1)$ patterns with no observable steps (e.g., no split spots).

In Fig. 1, EDC's are shown for USb(100), $U_{0.85}Th_{0.15}Sb(100)$, $U_{0.34}Th_{0.66}Sb(100)$, and ThSb(100) for $h\nu = 40$ eV. For the lower three spectra, the predominant emission near E_F is due to 5femission. Neutron scattering experiments⁷ of USb and photoemission studies⁸ of the USb_xTe_{1-x} system conclude that uranium has a U³⁺ valence state in USb, with a quasilocalized $5f^{3-8}6d^8$ ($\delta \approx 0-0.5$) level at E_F . The sharp, prominent 5f emission within ~ 0.5 eV of E_F is associated with this level; i.e., it represents the $5f^2$ final-state spectrum, with peaks B and C likely being multiplet peaks.⁹ An interesting trend is observed for the 5f, 6d conduction bands near E_F with increasing Th concentration which we

<u>24</u>

406



FIG. 1. Angle-integrated EDC's at hv = 40 eV for USb, U_{0.34}Th_{0.66}Sb, U_{0.85}Th_{0.15}Sb, and ThSb at room temperature. The curves are normalized to equal 5p valence-band heights assuming a filled valence band. The spectra are aligned so that the 5p peak heights coincide; this causes peaks *B* to coincide as well. The resulting relative shifts of E_F are given in eV. In the U_{0.34}Th_{0.66}Sb spectrum, a partial *d*-electron density of state is shown which is defined as $\frac{2}{3}$ that of the ThSb *d* spectrum.

have illustrated in Fig. 1 by keeping the dominant f peak B at a constant position and shifting the Fermi energy E_F . Namely, with increasing Th concentration, E_F moves upwards and the f-like spectral peaks B and C remain invariant at a *constant*-energy separation from the lower-lying Sb-derived valence bands (for U_{0.34}Th_{0.66}Sb, peak C is not resolved because of energy-dependent lifetime broadening⁸). As plotted in Fig. 1, E_F moves upwards by 0.46 \pm 0.02 eV from USb to ThSb. Thorium, with a $6d^26s^2$ atomic confi

guration, is expected to have three electrons associated with the filled valence bands and about one 6delectron in a metallic conduction band in ThSb; the latter is associated with the \sim 1-eV-wide metallic conduction band (feature A) near E_F in Fig. 1. In contrast with the results of a recent band-structure calculation,¹⁰ we observe a monotonic increase of E_F with increasing Th concentration with a filling of these bandlike 6d states. A rough estimate of the density of conduction-band states near E_F which become filled on going from USb to ThSb, n(E), is given by the Fermi-level movement; i.e., $n(E) \sim 1 e^{-1}/0.46 eV$ $\approx 2.2 \ e^{-}/eV$. This state density is only about $\frac{1}{2}$ that of a spin-polarized f band having an \sim 1.5-eV width,^{3,11} and thus as previously concluded,⁸ we find the 5f electrons to be better described by a quasilocalized resonant state than by a 5f bandlike state. A significant result is given by the fact that the predominant $5f^2$ final-state peak B in Fig. 1 is invariant in energy relative to the valence bands for U concentrations of $1 \ge x \ge 0.34$ and does not shift with Th concentration.

Additional evidence for the presence of 6d bandlike states near E_F for the entire system $U_x Th_{1-x}Sb$ for $0 \le x \le 1$ is shown in Fig. 2. Here we show EDC's for hv = 92 eV, a photon energy which corresponds to a pronounced resonance minimum $(\sim \frac{1}{100})$ in the 5*f* emission intensity [Ref. 12 and our results (unpublished)]. All spectra in Fig. 2 show a metallic edge at E_F which we attribute to occupied 6*d* electrons. For the $U_{0.34}Th_{0.66}Sb$ spectrum in Fig. 1, the spectral intensity of peak *A* is due to 5*f*-like emission, but contains a significant amount of 6*d*-like



FIG. 2. EDC's for USb, $U_{0.34}$ Th_{0.66}Sb, and ThSb at $h\nu = 92$ eV. This photon energy corresponds to a minimum of the 5*f* emission due to the 5*d* \rightarrow 5*f* resonant excitation (Ref. 12).

emission (estimated by the dashed line). At $h\nu = 40$ das eV, the 5*f*-like partial cross section per electron is estimated to be roughly twice as large as the 6*d* partial photo cross section. In addition, the intensity ratio of U_x^{-1}

photo cross section. In addition, the intensity ratio of the 5f peak B and 6d emission feature at E_F can be significantly varied near the 5f resonance minimum (see Fig. 2). This $h\nu$ -dependent ratio is also consistent with our identification of 5f and 6d levels. The 5f-like spectral intensity in peak A could be due to a resonant broadening of the predominant peak B due to the additional 6d conduction electrons. We can rule out a pure itinerant picture with 5f band filling, since the Fermi level movement would require very wide 5f bands ($\geq 3 \text{ eV}$).

We next discuss the interesting magnetic behavior of the $U_x Th_{1-x}Sb$ system in light of our finding that uranium retains a constant valence state. Recently, Cooper et al.⁵ have reported magnetization measurements and susceptibility measurements which show an interesting but complicated behavior: USb is an antiferromagnet ($T_N = 241.2$ K) with an ordered moment of 2.82 μ_B (4.2 K) along (100), while $U_x Th_{1-x}Sb$ becomes an ordered ferromagnet with a (111) easy axis for $0.83 \ge x \ge 0.3$. Figure 3 depicts (a) the remanent ordered moment M_0/μ_B for varying uranium concentration in $U_x Th_{1-x}Sb$ (circles), (b) a theoretical description of M_0/μ_B by Cooper et al.⁵ (dashed line), and (c) a new simple model based on our photoemission findings (solid curve, to be discussed). In the model of Cooper et al.,⁵ it is assumed that uranium is trivalent $[U^{3+}(5f^3)]$ for uranium concentrations x > 0.83 and undergoes a valence change at $x \leq 0.7$ to become tetravalent $[U^{4+}(5f^2)]$ in the ferromagnetic regime $x \leq 0.7$ with singlet-ground-state ferromagnetism as shown by the



FIG. 3. Ordered magnetic moment for varying uranium concentration in $U_x Th_{1-x}Sb$: (a) experiment, (b) theory of Cooper *et al.* (Ref. 5) assuming a $U^{4+}(f^2)$ configuration, and (c) our model [Eq. (1)] taking into account an antiparallel *d*-electron moment.

dashed line Fig. 3. In a more recent study¹³ of the magnetization of $U_x Y_{1-x}Sb$, Cooper *et al.* conclude that there may not be a valence change in $U_x Th_{1-x}Sb$, but that the valence state may be $U^{4+}(5f^2)$ for all uranium concentrations.

As discussed above, we find no valence change in $U_x Th_{1-x}Sb$ for $1.0 \ge x \ge 0.34$ and conclude that U remains trivalent with a quasilocalized $U^{3+}(5f^{3-\delta}6d^{\delta})$ configuration while Th essentially contributes approximately one 6d electron per Th to the conduction band. Additional insight is given by the fact that the magnetic behavior of $U_x Th_{1-x}Sb$ is similar to that of $USb_{x}Te_{1-x}$,¹⁴ which changes from an antiferromagnet for $x \ge 0.83$ to a ferromagnet for $0.83 \ge x \ge 0$. For USb_xTe_{1-x} , we have found⁸ the same 5*f* resonant state with a filling of *d*-like electrons at E_F with increasing Te concentration. Thus, in view of our findings, antiferromagnetic behavior with moments along $\langle 100 \rangle$ is only favored when the number of d electrons is small. Moreover, spin-polarized photoemission studies⁴ have shown these d electrons at E_F for UTe to be antiparallel to the ordered 5f moment and thus account for the lower ordered moment in UTe compared with USb. Based on the above, we conclude that 6d electrons play an important role in $U_x Th_{1-x}Sb$ which is similar to that in $USb_x Te_{1-x}$. Namely, for uranium concentrations $1 \ge x \ge 0.3$ in the ordered region, we suggest that the Th-derived 6delectron is polarized with a moment μ_d which is antiferromagnetically aligned relative to the U-derived moment μ_f . Assuming that the moment μ_d per Th is independent of concentration for $x \ge 0.3$, we have the simple result

$$\frac{M_0}{\mu_B} = \mu_f - \frac{1 - x}{x} \mu_d \quad . \tag{1}$$

This curve is plotted in Fig. 3 (solid line) for $\mu_f = 2.82 \mu_B$ (value for USb) and $\mu_d = 1.3 \mu_B$ (obtained by fitting to $U_{0.5}Th_{0.5}Sb$) and is seen to give a very good description for all concentrations $1 \ge x \ge 0.3$. The disappearance of the ordered moment at x = 0.3 corresponds to a cancellation of the U 5f moment by the antiparallel 6d moment. The above μ_f and μ_d moments are both ~80-85% as large as calculated for atomic $5f^3$ and $6d^1$ configurations, and they appear to be reasonable in view of crystal-field effects, etc. Within this model involving polarized 6d electrons, we suggest that the change from antiferromagnetism to ferromagnetism involves the 6d conduction electrons, possibly via a RKKYtype mechanism.¹⁵ We caution that our description of the magnetic behavior involves a very crude model (e.g., the 6d electrons are not localized and the 6d moment per Th cannot be independent of concentration as U is diluted) and must be viewed as a tentative description. Further experimental studies such as spin-polarized photoemission studies, neutron scattering measurements of 5f moments, and

theoretical studies of RKKY-type models should clarify further if our model is correct. Concerning the related system $U_xY_{1-x}Sb$ studied by Cooper *et al.*,¹³ its magnetic behavior appears to be consistent with our conclusion of an essentially trivalent $U^{3+}(5f^{3-8}6d^8)$ configuration rather than a tetravalent $U^{4+}(5f^2)$ configuration as previously suggested. Namely, Y is trivalent and is therefore less effective than Th in contributing *d* electrons; thus a significantly larger Y concentration is needed both for a transition to ferromagnetism (at $U_{0.5}Y_{0.5}Sb$) and for the disappearance of an ordered moment (at $U_{0.2}Y_{0.8}Sb$). In summary, we conclude that the lighter actinides are not only characterized by the 5*f* electrons, but that the 6d electrons are as unique in determining their electronic and magnetic properties.

ACKNOWLEDGMENTS

We are grateful for the excellent support from the Synchrotron Radiation Center and the many contributions of J. J. Donelon and A. Marx as well as fruitful discussions with J. F. Janak and V. Moruzzi. We thank K. Mattenberger for his help in growing the single crystals. This work was supported in part by the Air Force Office of Scientific Research under Contract No. F49620-80-C0025 and was sponsored by the Swiss National Science Foundation.

- ¹Physica (Utrecht) B <u>102</u> (1980) [Proceedings of International Symposium on the Physics of Actinides and Related 4fMaterials, Zürich, Switzerland, 9-11 April 1980, edited by P. Wachter].
- ²The Actinides: Electronic Structure and Related Properties, edited by A. J. Freeman and J. B. Darby, Jr. (Academic, New York, 1974).
- ³J. Schoenes, Phys. Rep. <u>66</u>, 187 (1980).
- ⁴B. Reihl, M. Erbudak, and F. Greuter, J. Magn. Magn. Mater. <u>13</u>, 132 (1979).
- ⁵B. R. Cooper, O. Vogt, and R. Siemann, J. Magn. Magn. Mater <u>15-18</u>, 1249 (1980).
- ⁶D. E. Eastman, J. J. Donelon, N. C. Hien, and F. J. Himpsel, Nucl. Instrum. Methods <u>172</u>, 327 (1980).
- ⁷G. H. Lander, M. H. Mueller, D. M. Sparlin, and O. Vogt, Phys. Rev. B 14, 5035 (1976).
- ⁸B. Reihl, N. Mårtensson, P. Heimann, D. E. Eastman, and O. Vogt, Phys. Rev. Lett. <u>46</u>, 1480 (1981).

- ⁹We can exclude the possibility of a tetravalent f^2 uranium initial-state configuration, since this would lead to a $5f^1$ final state with two spin-orbit components ($f_{7/2}$ and $f_{5/2}$) split by 0.94 eV [V. Kaufman and L. J. Radziemski, Jr., J. Opt. Soc. Am. <u>66</u>, 599 (1976)]. No sign of such a splitting is seen in any of our spectra.
- ¹⁰P. Weinberger and R. Podloucky, Phys. Rev. B <u>22</u>, 645 (1980); and Physica (Utrecht) B <u>102</u>, 59 (1980).
- ¹¹M. S. S. Brooks (private communication).
- ¹²R. Baptist, M. Belakhovsky, M. S. S. Brooks, R. Pinchaux, Y. Baer, and O. Vogt, Physica (Utrecht) B <u>102</u>, 63 (1980).
- ¹³B. R. Cooper, O. Vogt, and R. Siemann, Physica (Utrecht) B 102, 41 (1980).
- ¹⁴G. Busch, O. Vogt, A. Delapalme, and G. H. Lander, J. Phys. C <u>12</u>, 139 (1979).
- ¹⁵J. Grunzweig-Genossar, M. Kuznietz, and F. Friedman, Phys. Rev. <u>173</u>, 562 (1968).