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Itinerant-5f-electron antiferromagnetism in uranium nitride: A temperature-dependent angle-resolved photoemission study

B. Reihl
IBM Zurich Research Laboratory, CH-8803 Rüschlikon, Switzerland

G. Hollinger and F. J. Himpsel
IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598

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A 5f-like photoemission peak emerges at $E_F - 0.78$ eV in normal emission from UN(100) upon cooling below $T_{\mathrm{Néel}} = 53$ K. This is the first observation of its kind for f electrons. We believe that this peak arises from band states which are folded back into the new antiferromagnetic Brillouin zone owing to the doubling of the unit cell along ⟨100⟩. Isoelectronic USb, which has localized 5f electrons, does not exhibit such a temperature effect. Our results suggest that UN can be described within the theory of itinerant-5f-electron antiferromagnetism.

I. INTRODUCTION

Itinerant or bandlike electronic behavior is a fundamental solid-state property. It is best exemplified in the d transition-metal series, and band magnetism theory[1] can explain ferromagnetism in Fe, Co, and Ni, as well as antiferromagnetism in Cr.[2] Electronic itinerancy manifests itself experimentally by the existence of Fermi surfaces, effective electron masses, and energy-band dispersion in de Haas—van Alphen (dHvA) and angle-resolved photoemission experiments. Contrarily, f electrons in general do not exhibit such characteristics because of their strong spatial confinement around each nucleus (f localization). Instead, atomiclike f^n final-state multiplets occur in photoemission from rare-earth and actinide systems, and the ratio of the ordered and paramagnetic moments $\xi = \mu_0/\mu_p = [J/(J+1)]^{0.5}$ lies within well-defined limits given by the Hund's-rule coupling scheme.[3]

High effective masses due to f electrons have recently been found in $CeSn_3$.[4] dHvA measurements have also been performed on URh_3,[5] UGe_3,[6] and α-U,[7] but effective masses were smaller so that conclusions were possible only by comparison with band-structure calculations. The best-studied itinerant f system is UIr_3 for which a complete set of band-structure calculations is corroborated[8] by dHvA and angle-resolved photoemission data.[9] Finally, itinerant-5f-electron antiferromagnetism has been reported for $NpSn_3$ from specific-heat and Mössbauer measurements.[10]

Here we present[11] temperature-dependent angle-resolved photoemission results from the UN(100) surface, which suggest that f-like band states become manifest upon cooling UN below its Néel temperature $T_N = 53$ K.

Uranium nitride has the smallest U-U distance (3.46 Å) amongst the UX (X=N, P, As, Sb, S, Se, and Te) compounds and is close to the critical 3.4 Å given by Hill[12] for the onset of magnetism in actinide systems. All the other UX clearly fall into the localized regime. The magnetic properties of the UX compounds are summarized[13] in Table I together with the theoretical values for an f^3 ground-state configuration in Russel-Saunders coupling. In the last column of Table I, ξ ranges from 0.6 to 0.8 in going from UP to UTe, and is close to the f^3 value. The discrepancies reveal crystal-field effects[3] and the influence of the magnetic 6d electrons[14] neglected in Table I. The low $\xi = 0.28$ value for UN, however, does not follow the general trend, indicating a possible itinerant-5f-electron description in which μ_p would not be defined.[1,3] This anomaly of μ_0, or ξ, has motivated several groups to search for bandlike 5f-electronic behavior in UN. The most successful experiment so far was conducted by Fournier *et al.*,[15] who found that μ_0 and T_N obey the same pressure dependence, as required by itinerant antiferromagnetism theory.[2] Norton *et al.*[16] could not detect any differences in angle-integrated photoemission spectra taken above and below ~50 K. In an angle-resolved photoemission study at room temperature, Baptist *et al.*[17] did

TABLE I. Magnetic properties of UX compounds summarized with the theoretical values for an f^3 ground-state configuration in Russel-Saunders coupling (from Ref. 13).

UX	$d_{\text{U-U}}$ (Å)	T_N, T_c (K)	μ_0 (μ_B)	μ_p (μ_B)	$\xi = \mu_0/\mu_p$
UN	3.46	53	0.75	2.66	0.28
UP	3.95	123	2.0	3.35	0.60
UAs	4.08	127	2.24	3.4	0.66
USb	4.38	214	2.82	3.64	0.77
US	3.88	177	1.70	2.2	0.77
USe	4.06	160	2.0	2.5	0.80
UTe	4.35	102	2.25	2.8	0.80
f^3			3.27	3.62	0.90

not find any angular dependence of the 5f-emission peak at E_F, indicating there is no band dispersion $E(\vec{k})$.

From the theoretical point of view, *all* UX compounds have been treated within a band picture.[18,19] Recently, however, it has been shown that the 5f electrons appear to be localized in USb and UTe,[14] and UAs and USe,[20] and that bandlike 6d electrons with their moments antiparallel to the localized 5f moments can explain the magnetic properties (cf. Table I).

II. EXPERIMENT

The experiments were performed with the IBM two-dimensional spectrometer[21] using synchrotron radiation from the Tantalus I storage ring at the Synchrotron Radiation Center in Madison, Wisconsin. Single crystals of UN were mounted on a close-cycle ^{4}He cryostat which reached a temperature of $T=33$ K. The minimum temperature is uncertain by ± 3 K, while the error at higher T is estimated to be smaller than ± 10 K. The samples were cleaved at low temperature along their (100) planes in a vacuum of 1×10^{-10} Torr and immediately afterwards brought into measurement position (vacuum of 5×10^{-11} Torr) by lowering the whole cryostat. The overall resolution (electrons and photons) was set to $\Delta E<150$ meV yielding count rates of $\sim 10^6$ per s in the angle-integrated ($\Delta\theta=86°$ full cone of emission angles) and $\sim 5\times 10^4$ per s in the angle-resolved ($\Delta\theta=12°$) mode.

III. RESULTS AND DISCUSSION

Figure 1 compares angle-integrated photoemission energy-distribution curves (EDC's) for UN(100) and USb(100) (Ref. 20) at 33 K taken with photon energies $h\nu=25$ eV (dominant p valence-band emission) and $h\nu=40$ eV (dominant 5f emission). We note a big difference between UN and USb, namely, the latter clearly exhibits a 5f^2 final-state multiplet[22] as is well known from the localized 4f systems, while for UN we find a single 5f-emission peak cut by the Fermi level E_F, which is significantly wider than the 5f features in isoelectronic USb and UAs.[20] The substantially broader width in UN is taken as a first indication in photoemission that a bandlike 5f description is correct, which formally requires that the bandwidth W be sufficiently larger than the Coulomb correlation energy U. The angle-integrated EDC's in Fig. 1 resemble those taken at room temperature (not shown), the only difference being a sharpening of the peaks at 33 K owing to a less effective phonon broadening. This is consistent with the findings of Norton *et al.*,[16] who could not detect any changes with T in their angle-integrated x-ray photoemission spectroscopy (XPS) study. The differences in the 5f emission from UN and USb are still apparent at $h\nu=25$ eV [cf. Figs. 1(a) and 1(b)]. A weak shoulder at about -0.5 eV in the UN spectrum [Fig. 1(a)] urged us to perform a temperature-dependent angle-resolved study, the results of which suggest the itinerant character of the 5f electrons in UN and are now presented in detail.

Angle-resolved ($\Delta\theta=12°$) EDC's at $h\nu=25$ eV and normal emission ($\theta=0°$) are shown in Fig. 2 for temperatures

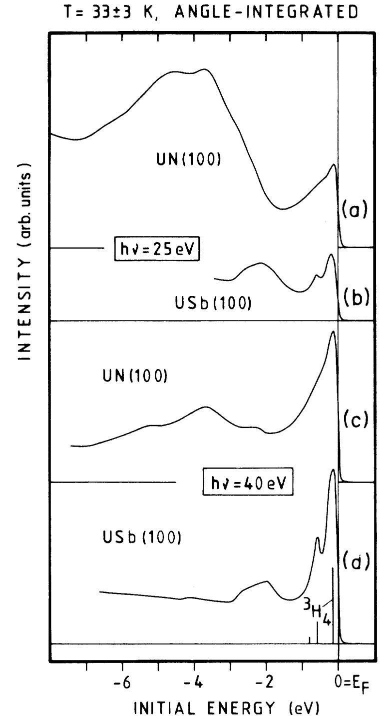

FIG. 1. Angle-integrated EDC's from UN and USb at $h\nu=25$ and 40 eV. From the $h\nu$ dependence it is clear (cf. Refs. 14 and 20) that the emission features near E_F have 5f character, while the features below -1.5 eV represent the anion-derived p valence bands (to be discussed elsewhere). The bar diagram in curve d represents an f^2 final-state multiplet ($^3H_4$, $^3F_2$, and $^3H_5$) as obtained from Ref. 22.

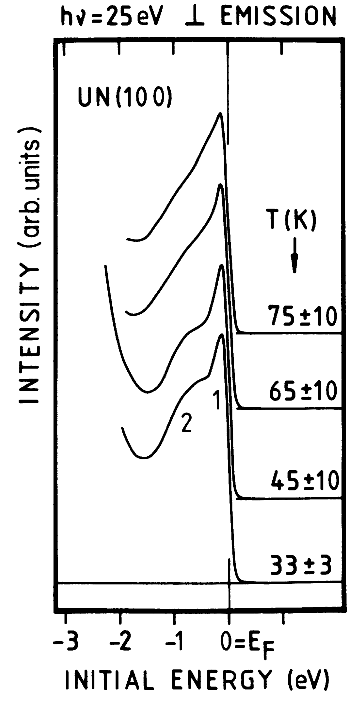

FIG. 2. Angle-resolved EDC's from UN(100) at $h\nu=25$ eV (mixed s,p polarization) and normal emission for various temperatures. Note the disappearance of peak 2 with increasing T. All curves were obtained within 15 min after the cryostat had been switched off.

ranging from 33–75 K. Normal emission was determined from the incoming and reflected light making use of the display-type spectrometer.[21] At low temperatures, we see a strong emission feature emerging at about −0.7 eV (denoted as peak 2) in addition to the sharp peak right at E_F (denoted as peak 1). Peak 1 showed hardly any dependence on the polar angle θ in agreement with Baptist *et al.*'s room-temperature results.[17] Peak 2 was strongest for $\theta=0°$ and $\Delta\theta \leq 12°$, but its intensity decreased with increasing $\theta > 6°$, which explains why we could hardly discern it in the angle-integrated EDC of Fig. 1(a). A search for band dispersion by varying the photon energy revealed an inherent difficulty in dealing with f electrons. Namely, medium to high photon energies are required to overcome the low f photoemission cross-section at lower $h\nu$, while substantial k broadening due to the short mean free path of photoelectrons in these heavy-Z materials destroys all $E(\vec{k})$ information at higher $h\nu$.[23] In this sense, $h\nu=25$ eV represents a compromise,[24] and the differences between the angle-integrated and the angle-resolved EDC's reveal the dispersive character of peak 2. Furthermore, in Fig. 2 we show what happened after the cryostat had been switched off and the temperature increased: Peak 2 decreased as T was raised above the Néel temperature. This effect was reversible as measured in several warming-up and cooling cycles.

To obtain peak positions more accurately, we have used the following procedure based on an itinerant picture: A "theoretical" function was composed using two Lorentzians of variable intensities I_1 and I_2, and full widths at half maximum W_1 and W_2, and a background function which took into account the p valence-band emission [cf. Fig. 1(a)] as well as secondary electron loss. This was multiplied by the Fermi function, and a least-squares routine was used to fit the experimental data. The peak positions were chosen to give the best-fit results for *all* curves at different temperatures. There is no physical reason to use T-dependent peak positions, as will be explained below. The quality of the fit and the decomposition into single contributions can be seen in Fig. 3, where normal-emission EDC's at three different temperatures are analyzed. We find peak 1 at −0.09 eV and peak 2 at −0.78 eV with $W_2 > W_1$ at all temperatures, as an energy-dependent lifetime broadening requires. Most striking is the increase of the intensity ratio $R=I_1W_1/I_2W_2$ from $R=1.37$ at 33 K to 2.43 at 75 K. This will now be discussed in terms of the antiferromagnetic phase transition in UN.

To the best of our knowledge, there exist only paramagnetic band-structure calculations[18,19] for UN. To obtain at least a qualitative understanding, we have schematically derived the antiferromagnetic band states from the paramagnetic states in analogy[25] to the itinerant 3d antiferromagnet chromium. UN is a rocksalt type-I antiferromagnet[13] characterized by (001) ferromagnetic sheets stacked in an alternating + − + − sequence. The moment direction is perpendicular to the sheets. Within each domain, the fcc unit cell is doubled along one particular ⟨100⟩ direction upon cooling through T_N, which results in a new antiferromagnetic Brillouin zone of half the size along this ⟨100⟩ axis. The energy bands are altered in two ways (see Fig. 4): (i) band states along ΓX are folded back into the new antiferromagnetic Brillouin zone creating new states at Γ, and (ii) degeneracies at the new zone boundary (0.5 X in Fig. 4) are lifted producing energy gaps.

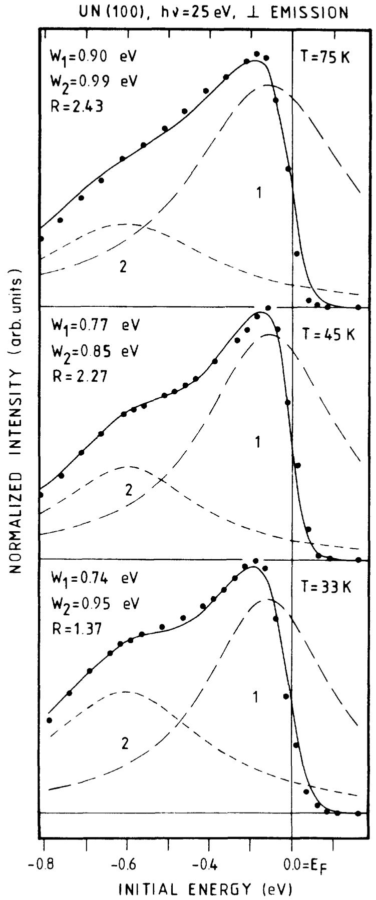

FIG. 3. Angle-resolved EDC's from UN(100) at $h\nu=25$ eV and normal emission. The black dots represent the experimental data after background subtraction. Solid lines indicate the fitted theoretical functions (see text) and their decomposition into two Lorentzians (widths W_1 and W_2, intensity ratio $R=I_1W_1/I_2W_2$) at the following energies: Peak 1, −0.09 eV; peak 2, −0.78 eV.

To illustrate this, in Fig. 4 we have reproduced the occupied part of the 5f bands of UN as calculated by Weinberger *et al.*[18] and by Brooks.[19] Both calculations produce similar 5f bands which, however, are much flatter (corresponding to a smaller bandwidth) in Brooks's calculations. In Fig. 4 we have taken these differences into account by using two different energy scales. For $T > T_N$ and $h\nu=25$ eV, we get emission from Γ_7^- into a free-electron-like final-state band (not shown), which we attribute to peak 1 (cf. Fig. 2). *In addition*, for $T \leq T_N$, we could get emission from the band-gap states at the new antiferromagnetic zone boundary (0.5X in Fig. 4), which would produce a peak at about −3 eV in the band structure of Weinberger *et al.*, and at about −1.5 eV in Brooks' calculation. The fact that we observe peak 2 at a different energy (−0.78 eV) indicates that both paramagnetic band-structure calculations[18,19] (apart from being inconsistent with each other) cannot be used in the same manner as in chromium[25] to obtain the antiferromagnetic bands. Namely, band states

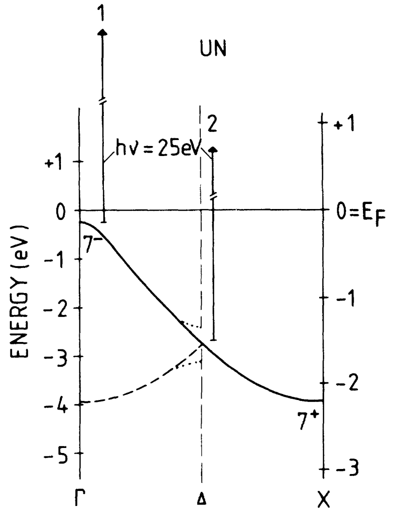

FIG. 4. Schematic reproduction of the paramagnetic occupied 5f-band states along ΓX (solid line) from Ref. 18 (left energy scale) and Ref. 19 (right energy scale). In the antiferromagnetic phase, the band is folded back (dashed line) into the new Brillouin zone, creating a new state at Γ and an energy gap (dotted lines) at the new zone boundary ($0.5k_{\Gamma X}$). Peak 1 is attributed to emission at $h\nu = 25$ eV (arrows) into a free-electron-like final state, while peak 2 could arise from the band-gap states.

along XW also change and produce additional new states and gaps which could modify our schematic interpretation which we confined to the ⟨100⟩ direction (ΓX), since XW was not calculated in Refs. 18 and 19. A fully antiferromagnetic band-structure calculation is clearly needed.

Ideally, peak 2 should disappear completely in the spectra when going from the antiferromagnetic to the paramagnetic phase $T > T_N = 53$ K. However, as in chromium,[25] we still get a contribution for peak 2 at $T > T_N$ (cf. Figs. 2 and 3), which we attribute to short-range spin correlations[26] that persist above the Néel temperature. This conclusion goes along with the recently observed persistence above T_c of the magnetic photoemission peaks in Ni.[27]

IV. SUMMARY

We have observed a photoemission peak in normal emission from UN(100), which emerges when cooling UN below its Néel temperature. This is in contrast to isoelectronic UAs and USb, both of which exhibit a $5f^2$ final-state multiplet that becomes continuously sharper upon cooling. An attempt has been made to qualitatively correlate the temperature-dependent emission feature in UN with band states folded back into the new antiferromagnetic Brillouin zone for $T < T_N$. For a quantitative analysis, an antiferromagnetic band-structure calculation is necessary. Still, we take our experimental result on UN and its contrasting behavior to UAs and USb as suggestive of itinerant-5f-electronic behavior in UN, while UAs and USb have localized 5f electrons as previously concluded. Thus the anomalous moment in UN as compared to the other UX compounds may manifest itself directly in the electronic structure.

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EDC's became identical for $h\nu \gtrsim 40$ eV. On cleaved surfaces, such as UN(100), irregularities, steps, etc. provide additional k-broadening mechanisms.

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