Imaging of $5f$ densities of states in resonant photoemission measurements

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Medium-resolution spectra ($\Delta E = 0.25$ eV) at the $5f$ Fano resonance in uranium intermetallics are compared to spectra above and below the resonance region to show that the $5f$ (and $6d$) spectral weight obtained from resonant photoemission (RP) compares well to the $5f$ spectral weight obtained at other photon energies. In well-hybridized systems, the $5f$ signal from RP gives an excellent representation of the $5f$ density of states (DOS). In narrow-band and localized systems, a satellite may appear in addition to $5f$ DOS-like structure, indicative of correlation effects.

I. INTRODUCTION

A recent publication[1] (SHCZ) has questioned the accuracy of deducing $5f$ bandwidths in uranium intermetallic compounds from resonant photoemission (RP) measurements. They propose that a resonant Auger transition at RP broadens experimental widths. This is indeed an important question owing to the interest in this information stimulated by heavy-fermion systems.[2,3] Understanding the systematics of $5f$ bandwidths may yield insight into heavy-fermion behavior.[4]

RP is understood as an atomic process as first described by Fano[5] to explain line shapes in core absorption edges. At an excitation threshold, a strong additional channel opens up for $5f$ emission which interferes with the normal photoemission channel. In the case of uranium, the excitation is a $5d$ transition at $h\nu = 94$ eV. $5d$ electrons are pumped into empty $5f$ states just above E_F where they are trapped in the angular momentum barrier.[6] As they decay back to refill the $5d$ hole, they selectively emit another $5f$ electron from a filled state via a super-Coster-Kronig (SCK) autoionization process. Clearly, other processes are also possible, although with lower probability, including (1) the emission of a $6d$ electron,[7] or Coster-Kronig (CK) autoionization and (2) a resonant Auger process[8–10] whereby the $5d$ hole is filled by a valence $5f$ electron accompanied by the emission of another valence $5f$ electron. This latter process (which is pinned at E_F) has been suggested by SHCZ to preclude the use of RP to observe $5f$ character. It differs from SCK (which presumably reflects the $5f$ directly) in that the line shape is a self-convolution of the valence band (i.e., twice as broad). Analyses of RP experiments[11,12] have assumed that the latter process is negligible. In this paper we will show that this is indeed the case. Parenthetically, why the SCK process works as well as it does for *bandlike* $5f$ systems to selectively pick out $5f$ (and some $6d$) emission is a question that still requires further theoretical investigation. Our present observations regarding RP in uranium compounds directly contradict SHCZ who claim that in well-hybridized $5f$ systems a resonant Auger channel does accompany the other channels of decay and may account for up to 50% of the spectral weight. The resulting corollary that the $5f$ photocurrent from RP does not image the $5f$ density of states (DOS) in well-hybridized $5f$ bands would be so significant that this assertion requires careful scrutiny. We believe it is differences in resolution, coupled with difficulties in properly normalizing the off-resonance and on-resonance spectra (particularly in USi_3) that form the basis for the difference in interpretation. Here it will be demonstrated that RP is indeed a useful tool.

We have utilized RP measurements extensively since we have been interested in accurately measuring the electronic structure of $5f$ systems.[13–16] In this paper we report studies on a number of materials at photon energies ranging from 40 to 124 eV, completely spanning the RP region (92–108 eV). This includes several systems (UGe_3, UBe_{13}, USi_3) discussed by SHCZ. It is observed that in systems where the ligand signal is not too strong (UGe_3, USi_3, UBe_{13}), the $5f$ photocurrent obtained with RP completely matches that obtained at lower energies (e.g., 40 eV). However, while the spectra at 40 eV and at RP are quite similar (indicating they reveal similar information) it is a very separate issue whether they necessarily image the $5f$ DOS. We find that in well-hybridized $5f$ systems (USi_3, UGe_3, URh_3, UIr_3) the match between calculated $5f$ DOS and photoemission is excellent. In nearly localized (UBe_{13}, UPt_3) and localized cases ($UPd_{3-x}Pt_x$), we believe an additional satellite is evi-

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denced,[16-17] the origin of which is still to be fully determined. However, our purpose here is to demonstrate that RP is indeed reflecting the direct structure unclouded by the Auger mechanism proposed by SHCZ.

II. EXPERIMENT

Measurements on UBe_{13} were carried out at the Tantalus synchrotron in Stoughton, Wisconsin using a Grasshopper monochromator, while the remaining measurements were done on the U2 beamline at the NSLS in Brookhaven using an ERG monochromator. The UBe_{13} measurements were done at low temperatures (20 K) so that the true instrument resolution can be directly deduced from the sharpness of the Fermi edge.[18] For the remaining measurements, which were performed at room temperature, one must account for kT broadening. In all cases, our instrument resolution determined from the Fermi edge was never worse than 0.3 eV. Samples were prepared in the usual manner by arc-melting the constituents, annealing the resulting buttons, and characterizing the samples by powder-diffraction measurements to verify single phase. They were cleaved *in situ* to expose a clean surface. The resonant part of the spectrum was obtained by subtracting the spectrum at antiresonance (92 eV) from that at resonance (99 or 108 eV). Before subtracting spectra, it was found useful to first subtract out the secondary background. This was done in the usual manner by assuming that the background at each binding energy is proportional to the total integrated signal at lower binding energies.[19] This has a slight but noticeable effect on the $5f$ bandwidth. Failure to thus account for background can in some cases result in improper normalization and hence $5f$ bandwidths that are too large.

III. RESULTS AND DISCUSSION

As examples of well-hybridized $5f$ systems, Figs. 1(a) and 1(b) show raw data for UGe_3 (at $h\nu=63$, 99, and 124 eV) and USi_3 (at $h\nu=40$ and 108 eV). These materials are actually ideal compounds for analysis because both the germanium and silicon *s-p*-like emission is extremely weak at and above $h\nu=40$ eV. Thus, even at energies far from resonance, the photocurrent is primarily due to U $5f$ and $6d$ emission. This enables direct comparison of spectra at different $h\nu$. The analysis of UGe_3 is discussed first since SHCZ also conclude that there is no evidence for an Auger broadening in UGe_3. (They choose to class it as a more localized system. This is not valid as it is certainly better hybridized than the heavy-fermion material UBe_{13} and almost as much so as USi_3 discussed below. The Fermi surface of UGe_3 has been completely determined[13] via the de Haas–van Alphen effect. The effective mass $m^* \leq 4$ for all orbits, which is even smaller than in URh_3.) In Fig. 1(a) the RP difference curve (a) is seen to represent well the $5f$ (strong peak at E_F) and $6d$ (tailing out to ≈ -5 eV) emission for UGe_3. The width of the $5f$ derived peak appears to be ≈ 0.85 eV in the raw data but is reduced to ≈ 0.7 eV in the difference curve. This narrowing is primarily a consequence of removal of the background. All widths shown are substantially smaller than previously observed[20] value of 1.9 eV, and are a consequence of improved resolution. Except for minor differences possibly attributable to minor changes in surface cleanliness between sweeps (a small amount of UO_2 formation will add intensity at -1.5 eV) and relative d- versus f-electron cross section, all spectra are essentially identical. A self-convolution of the $5f$ bandwidth could produce an Auger feature $\approx 2-4$ eV wide (possibly 8 eV wide if we include $6d$ electrons) so the similarity of these data implies that the Auger channel must be very weak.

The raw USi_3 spectra are slightly broader [≈ 0.9 eV full width at half maximum (FWHM)] than the UGe_3 spectra as should be expected from the slightly stronger hybridization. On the other band, they are considerably narrower than previous x-ray photoemission spectroscopy (XPS) results,[21] again reflecting improved resolution. Note that the 40-eV spectrum is essentially identical to the 108-eV spectrum with only minor differences emphasized by the difference curve. Both spectra are also

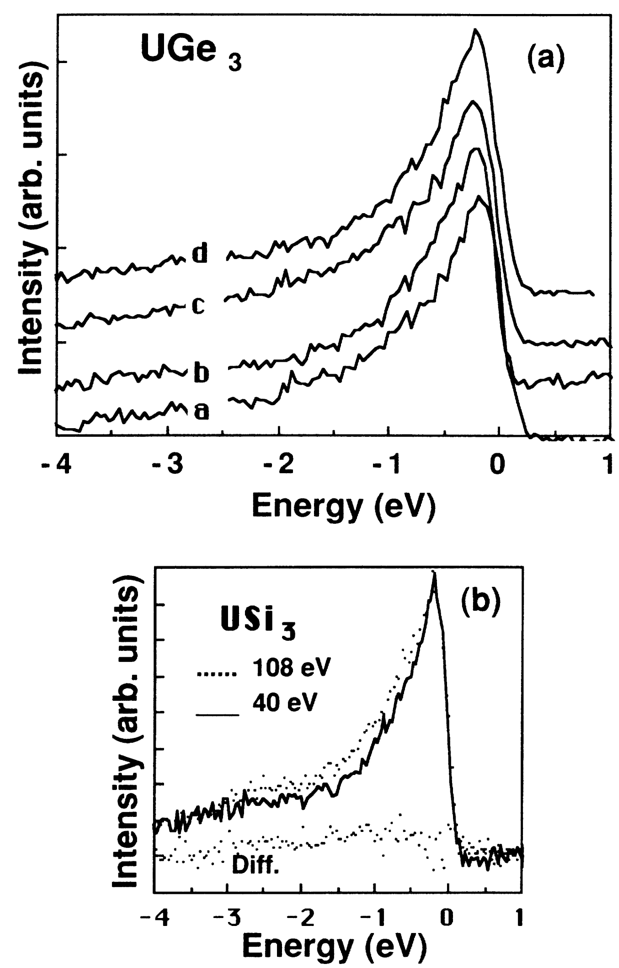

FIG. 1. (a) Photoemission spectra for UGe_3 with background removed. The difference curve a (resonance minus antiresonance) is nearly identical to the direct spectra (curve b, 63 eV; curve c, 99 eV; curve d, 124 eV) because the Ge p emission is so weak. (b) Comparison of the photoemission spectra for USi_3 at 40 and 108 eV.

similar to the previous XPS data once differences in resolution are accounted for. The XPS data have previously been shown to be consistent[22] with a calculated band-structure DOS. Consequently, the RP data must be consistent with band calculations as well. An RP subtracted curve is not shown for USi_3 because of difficulties encountered in establishing the normalization. A strong silicon Auger peak at ≈ 88 eV kinetic energy appears in the resonance region.[23] Failure to subtract it out prior to analyzing the $5f$ data will result in erroneous $5f$ widths. The raw UGe_3 and USi_3 data are so similar, however, that one must believe that the subtracted spectra would also be similar albeit slightly broader for USi_3 (perhaps 0.9 eV at FWHM). While not shown, the data for the extremely well-hybridized $5f$ compounds URh_3 and UIr_3 likewise exhibit agreement[13,14] between the observed $5f$ photospectrum and the $5f$ DOS. The evidence is thus quite strong that any Auger contribution is extremely weak in the well-hybridized materials.

Possibly, there is a slight hint of extra intensity for both UGe_3 and USi_3 in the -1 to -2 eV range in the on-resonance spectra [shown by the difference curve in Fig. 1(b)]. Because it is so weak one should be cautious in attributing it to a resonant Auger feature. It could be accounted for by differences in either cross section or resolution between the two photon energies. In any case, there is a similar suggestion of extra intensity in the XPS spectra,[21,22] where the Auger feature is not in question.

Because the interpretation of RP depends on the subtraction of data, one must be very careful about the normalization of data. It is a mistake to normalize at a sharp peak when comparing data of different resolutions. Since the $5f$ band density is a very sharp structure in the above spectra, the effect of instrument resolution will be quite profound. Poorer resolution will primarily result in a diminution of the sharp peak intensity at E_F. In this case, normalization at the secondary background is much better if the samples are clean. Figure 2 demonstrates the effect of resolution by superimposing the present USi_3 data ($\Delta E = 0.25$ eV) on data[1] with $\Delta E \approx 1.0$ eV. The spectra are normalized on the background. Clearly, the measured FWHM is a strong function of resolution.

We next examine UBe_{13} which is a heavy-fermion material and thus should be classed as a nearly localized or at least a weakly hybridized material[2]—certainly not as a well-hybridized material.[1] It too is a material well suited for analysis since previous measurements[24,25] have shown that the beryllium p emission is also quite weak compared to the uranium $5f$ or $6d$ emission. Figure 3 compares a theoretical curve[26] (solid line) and two experimental curves. The dashed curve is the RP difference curve using the 99-eV resonance, and the dotted curve is the raw 40-eV spectrum (taken at 20 K) but with the background subtracted out. The spectra were normalized at -1 eV. For the sake of clarification, the 40-eV spectrum is actually a composite of two spectra at different resolutions. Below -1.0 eV (where no sharp features are observed) the dotted 40-eV spectrum was taken with $\Delta E = 0.3$ eV to emulate the resolution existing at $h\nu = 99$ eV, and it is then joined to a spectrum taken with 0.09 eV resolution[18] above -1 eV. The reason for this is that with $\Delta E = 0.3$

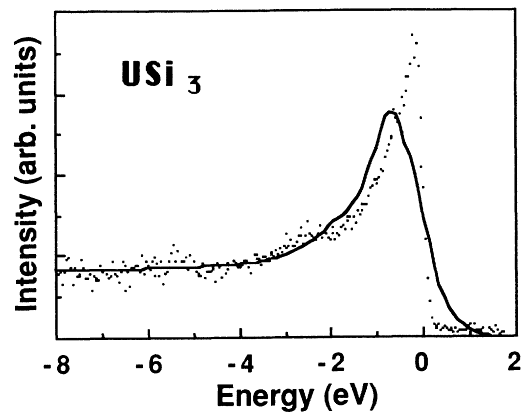

FIG. 2. Comparison of USi_3 spectrum having $\Delta E = 0.25$ eV (dotted curve) with one having $\Delta E = 1.0$ eV at the 108-eV resonance (from Ref. 1). Spectra were normalized on the secondary tail since differences in resolution are too great to allow normalization at the sharp peak. The differences in the spectra can be accounted for by differences in resolution.

eV, the very sharp peak at E_F is completely washed out even at $h\nu = 40$ eV. The 99-eV RP data and the 40-eV data are seen to differ mainly by the effects of resolution. Data obtained[27] for $h\nu = 108$ eV (not shown) are nearly identical to, and possibly even very slightly *narrower* than, the 99-eV data. Hence, again the evidence is for *no sign of an additional Auger broadening appearing at resonance.* Especially in UBe_{13}, it is essential to avoid normalization at the very sharp peak at E_F when comparing data of different resolution.

The two experimental UBe_{13} curves in Fig. 3 are obviously substantially broader than the theoretical curve.

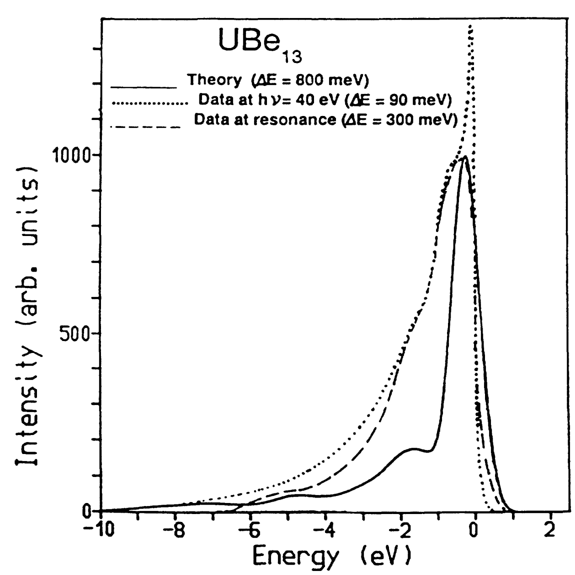

FIG. 3. Photoemission spectra for UBe_{13} compared to a broadened theoretical DOS. Dashed curve is the RP difference curve ($5f$ and $6d$ emission) and dotted curve is a composite spectrum for $h\nu = 40$ eV with background subtracted. The sharp peak at E_F is unobservable for a resolution $\Delta E \approx 0.3$ eV (see text).

The theoretical curve, constructed by convoluting the partial densities of states with the respective transition probabilities and further convoluting with instrumental broading (a Gaussian of 0.8 eV width), is the direct band-structure result. Much of the apparent large width of the experimental $5f$ DOS in UBe_{13} is then actually a consequence of U $6d$ emission. There is still, however, extra intensity observed in the -1-eV region as a consequence of correlation. Allen *et al.*[28] were first to point out this correlation intensity in UAl_2 and UPt_3. While they saw it only as a tailing of $5f$ spectral weight to higher binding energies, we have suggested[16,17] it to be a due to a well-defined $5f$ satellite centered at ≈ -1 eV, which would appear with increasing intensity as the $5f$ states become more localized. Subsequently, the extra intensity has been noted by others.[29,30] The spectra then consist of a blurred image of the $5f$ DOS admixed with a weaker image of the $6d$ DOS plus this additional satellite. This proposed satellite structure is *observed at all photon energies,* however, and hence cannot be an Auger feature.

Finally, we consider the localized system $UPd_{3-x}Pt_x$. Neutron diffraction data,[31] coupled with the specific-heat data,[32] clearly demonstrate the localized nature of $5f$ electrons in UPd_3. Baer *et al.*[33] have demonstrated that the photoemission fingerprint for localized $5f$ behavior in UPd_3 is the lack of $5f$ intensity at E_F. This fingerprint is observed for almost the entire range of x (up to $x = 2.6$). The arguments of SHCZ suggest that there should be no resonant Auger transition for localized systems. Yet the data for the $UPd_{3-x}Pt_x$ system show evidence for additional (satellite) intensity at 1.5 eV. The spectra in Fig. 4 are difference spectra (99–92 and 124–92 eV) for the $x = 0.025$ sample. Note that they are again very similar. The feature at -6 eV is a resonant feature (not related to any Auger transition) possibly due to $6d$ emission. It is *not* the satellite discussed above. In compounds where the ligand atoms (Pd and Pt) contribute substantial d spectral weight, resonating U $6d$ intensity is often normalized out (i.e., it usually mimics the ligand d DOS). but that does not appear to be happening here. The feature is, in any case, not directly related to the current question. This alloy system is particularly useful because at $UPd_{1.5}Pt_{1.5}$ a double peak structure is clearly distinguishable without requiring careful data manipulation. The entire series has been extensively studied and will be reported in full elsewhere.[34] Based on analysis of that data, we may note here that the "localized $5f$ peak" in Fig. 4, apparently centered at ≈ -1 eV, is actually composed of a main peak centered at ≈ -0.6 eV and a satellite centered at ≈ -1.1 eV. This produces the large width and the asymmetric line shape tailing off to higher binding energy. This structure again appears for all photon energies and should not be ascribed to an Auger process. Nonetheless, contrary to the analysis of SHCZ a broadening or actual additional peak *is* observed in these localized systems although the source is different from that discussed by SHCZ.

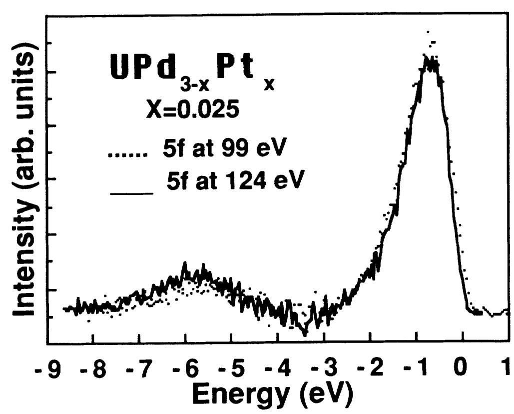

FIG. 4. $5f$ intensities (for the $x = 0.025$ sample) obtained by subtracting the spectrum for $h\nu = 92$ eV from spectra for $h\nu = 99$ and 124 eV. Data were normalized on a d peak at ≈ -4 eV. The $5f$ spectral weights obtained at the two photon energies are identical, indicating no resonant Auger peaks.

In conclusion we reiterate that the $5f$ line shape obtained at resonance in uranium compounds accurately matches the $5f$ lineshape obtained for photon energies away from resonance. There is, at best, weak evidence for a resonant Auger channel having measurable strength in any system that we studied. Some of the reported broadening in RP experiments (versus higher or lower $h\nu$) may be simply due to instrument broadening, combined with an improper subtraction of the background. Whether the line shapes image the $5f$ DOS is a separate question. That imaging appears to be quite good in well-hybridized $5f$ systems but not in very-narrow-band systems. In any case, one can always pick out the $5f$-$6d$ portion of the photocurrent by doing a resonance experiment with the exception that the $6d$ DOS is often subtracted out in compounds with transition metals.

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[1]D. D. Sarma, F. U. Hillebrecht, C. Carbone, and A. Zangwill, Phys. Rev. B **36**, 2916 (1987).
[2]P. A. Lee, T. M. Rice, J. W. Serene, L. J. Sham, and J. W. Wilkins, Comments Condens. Mater. Phys. **12**, 99 (1986).
[3]G. R. Stewart, Rev. Mod. Phys. **56**, 755 (1984).
[4]D. D. Koelling, B. D. Dunlap, and G. W. Crabtree, Phys. Rev. B **31**, 4966 (1985).
[5]U. Fano, Phys. Rev. **124**, 1886 (1961).
[6]J. L. Dehmer, A. F. Starace, U. Fano, J. Sugar, and J. W. Cooper, Phys. Rev. Lett. **26**, 1521 (1971).
[7]L. C. Davis and L. A. Feldkamp, Phys. Rev. B **23**, 6239 (1981), and references therein.

[8]W. Eberhardt, G. Kalkoffen, and C. Kunz, Phys. Rev. Lett. **41**, 156 (1978).

[9]M. Aono, T.-C. Chiang, J. H. Weaver, and D. E. Eastman, Solid State Commun. **39**, 1057 (1981).

[10]A. Fujimori and J. H. Weaver, Phys. Rev. B **31**, 6411 (1985).

[11]See, for example, Y. Baer in *Handbook of the Physics and Chemistry of the Actinides,* edited by A. J. Freeman and G. H. Lander (North-Holland, Amsterdam, 1984), Vol. 1, pp. 271–339.

[12]B. Reihl, N. Mårtensson, D. E. Eastman, A. J. Arko, and O. Vogt, Phys. Rev. B **26**, 1842 (1982).

[13]A. J. Arko, D. D. Koelling, and J. E. Schirber, in the *Handbook of the Physics and Chemistry of the Actinides,* Ref. 11, Vol. 2, p. 175.

[14]A. J. Arko, D. D. Koelling, and B. Reihl, Phys. Rev. B **27**, 3955 (1983).

[15]A. J. Arko, D. D. Koelling, A. M. Boring, W. P. Ellis, and L. E. Cox, J. Less-Common Met. **122**, 95 (1986).

[16]A. J. Arko, B. W. Yates, B. D. Dunlap, D. D. Koelling, A. W. Mitchell, D. J. Lam, Z. Zołnierek, C. G. Olson, Z. Fisk, J. L. Smith, and M. del Giudice, J. Less-Common Met. **133**, 87 (1987).

[17]A. J. Arko, B. W. Yates, B. D. Dunlap, D. D. Koelling, C. G. Olson, Z. Fisk, J. L. Smith, and M. del Giudice, in Proceedings of the Fourth International Conference on Valence Fluctuations, Bangalore, India, 1987 (unpublished).

[18]A. J. Arko, C. G. Olson, D. M. Wieliczka, Z. Fisk, and J. L. Smith, Phys. Rev. Lett. **53**, 2050 (1984).

[19]J. W. Allen, S. J. Oh, O. Gunnarson, K. Schonhammer, M. B. Maple, M. S. Torikachlivi, and I. Lindau, Adv. Phys. **35**, 275 (1986).

[20]F. U. Hillebrecht and D. D. Sarma (unpublished).

[21]D. D. Sarma, F. U. Hillebrecht, W. Speier, N. Mårtensson, and D. D. Koelling, Phys. Rev. Lett. **57**, 2215 (1986).

[22]D. D. Sarma, S. Krummacher, F. U. Hillebrecht, and D. D. Koelling (unpublished).

[23]*Handbook of Auger Electron Spectroscopy,* edited by L. E. Davis, N. C. MacDonald, P. W. Palmberg, G. E. Riach, and R. E. Weber (Perkin-Elmer Corp., Eden Prairie, MN, 1978), p. 51.

[24]G. Landgren, Y. Jugnet, J. F. Morar, A. J. Arko, Z. Fisk, J. L. Smith, H. R. Ott, and B. Reihl, Phys. Rev. B **29**, 493 (1984).

[25]E. Wuilloud, Y. Baer, H. R. Ott, Z. Fisk, and J. L. Smith, Phys. Rev. B **29**, 5228 (1984).

[26]A. M. Boring, R. C. Albers, G. Schadler, P. Marksteiner, and P. Weinberger, Phys. Rev. B **35**, 2447 (1987).

[27]A. J. Arko, C. G. Olson, and D. M. Wieliczka (unpublished).

[28]J. W. Allen, S.-J. Oh, L. E. Cox, W. P. Ellis, M. S. Wire, Z. Fisk, J. L. Smith, B. B. Pate, I. Lindau, and A. J. Arko, Phys. Rev. Lett. **54**, 2635 (1985).

[29]W.-D. Schneider, C. Laubschat, and B. Reihl, Phys. Rev. B **35**, 7922 (1987).

[30]J.-S. Kang, J. W. Allen, M. B. Maple, M. S. Torikachlivi, B. Pate, W. P. Ellis, and I. Lindau, Phys. Rev. Lett. **59**, 493 (1987).

[31]A. F. Murray and W. J. L. Buyers, *Crystalline Electric Field and Structural Effects in f-Electron Systems,* edited by J. E. Crow, R. P. Geurtin, and T. W. Mihalisin (Plenum, New York, 1980), p. 257.

[32]K. Andres, D. Davidov, P. Dernier, F. Hsu, W. A. Reed, and G. J. Nieuwenhuys, Solid State Commun. **28**, 405 (1978).

[33]Y. Baer, H. R. Ott, and K. Andres, Solid State Commun. **36**, 387 (1980).

[34]A. J. Arko, D. D. Koelling, B. D. Dunlap, A. W. Mitchell, C. Capasso, and M. del Guidice, J. Appl. Phys. **63**, 3680 (1988).