

Highly resolved surface shifts in a mixed-valent system: EuPd_2Si_2

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Synchrotron-radiation-excited photoelectron spectroscopy is employed to study the bulk and surface states of the mixed-valent system EuPd_2Si_2 , which undergoes a valence transition from $\text{Eu}^{2.2+}$ at room temperature to $\text{Eu}^{2.9+}$ at low temperature (≤ 100 K). The high resolution employed, coupled with a relatively large bulk-to-surface energy shift to the Eu^{2+} emission, allows a definitive identification of the bulk and surface states of Eu^{2+} . The Eu^{3+} emission is not observed at room temperature, but is readily apparent in the low-temperature spectra.

With increasing frequency, surface effects are being reported in photoemission studies of mixed-valent (or nearly mixed-valent) systems. The first such reported observation was that the surface of Sm metal is largely divalent, whereas the bulk is trivalent.¹ More recent studies (or interpretations) have suggested the presence of both a bulk and energy-shifted surface spectral component for the same initial state configuration, that state being Sm^{2+} (or $4f^6$), Tm^{2+} , Eu^{2+} , Yb^{2+} , or Ce^{3+} (or $4f^1$), found, e.g., in SmB_6 ,² SmS ,³ SmSe ,³ TmSe ,⁴ YbAl_3 ,⁵ and CeN .³ In all of these studies, except perhaps for CeN , the convolution of the spectra permitted only a qualitative estimate for the energy of the surface shift. The present results differ from previous work in that the spectral features associated with the surface shift are well separated and highly resolved, thereby permitting an accurate determination of the energy of the shift. Moreover, the rapid change of the bulk valence in EuPd_2Si_2 with temperature allows the study of the interplay between surface and volume states.

EuPd_2Si_2 crystallizes in the tetragonal TbCr_2Si_2 -type structure,⁶ wherein the Eu atoms reside on planes well separated by layers composed of the Pd and Si atoms. It is unique among the few Eu-based mixed-valent systems studied to date (viz., EuCu_2Si_2 , EuFe_4Al_8 , and EuRh_2)⁷ in that it undergoes a strong, albeit continuous, valence transition with temperature. The characterization of the valence transition by Mössbauer, magnetic susceptibility, and lattice constant measurements is reported in Ref. 8. The Mössbauer isomer-shift measurements indicate that the system is homogeneously mixed valent at all temperatures, with the valence varying from ~ 2.2 above the transition (whose midpoint is at ~ 150 K) to ~ 2.9 below. At least 90% of the valence change takes place within plus and minus 50 K from the midpoint.

Photoemission measurements were made with a display-type analyzer⁹ using synchrotron radiation at the University of Wisconsin, Madison. The system was operated in an angle-integrated mode with a total energy resolution of ~ 0.15 eV at 70-eV and ~ 0.3 eV at 120-eV photon energy. The measurements were made at 300 and 50 K on freshly fractured crystals in a vacuum better than 10^{-10} Torr. No signs of oxygen or other contaminants were seen during the course of the measurements.

Figure 1(a) shows the spectrum of EuPd_2Si_2 recorded at 50 K with a photon energy of $h\nu = 70$ eV. The spectrum is dominated by a relatively narrow Pd $4d$ band centered ~ 3.5 eV below E_F . Closer to the Fermi level there are two structures separated by 1.1–1.2 eV which we interpret as the bulk and surface Eu $4f$ emission from Eu^{2+} ions. In the energy range 6–10 eV, where we expect the trivalent Eu multiplets to occur, especially in this low-temperature phase which has a valence of 2.9, only a few very weak structures might be discerned. In order to make the Eu $4f$ emission more dominant in the spectrum, we can utilize the well-known fact that the Pd $4d$ emission has a Cooper minimum at photon energies around 120 eV.¹⁰ In Figs. 1(b) and 1(c) the spectra at 300 and 50 K are compared at this photon energy. The Pd $4d$ emission is now almost completely suppressed and the Eu $4f$ emission dominates the spectrum. Owing to the reduction of the Pd $4d$ emission, the trivalent multiplets in the 50-K spectrum are clearly seen. With this clearer view of the spectrum the interpretation is now more obvious. Closest to the Fermi level we find the bulk emission from Eu^{2+} ions corresponding to the excitation $f^7(5d6s)^2 \rightarrow f^6(5d6s)^3$, wherein the final state is fully screened. The lowest-lying multiplet line falls in the near vicinity of the Fermi level which is a necessary condition for homogeneous mixed valency, i.e., that

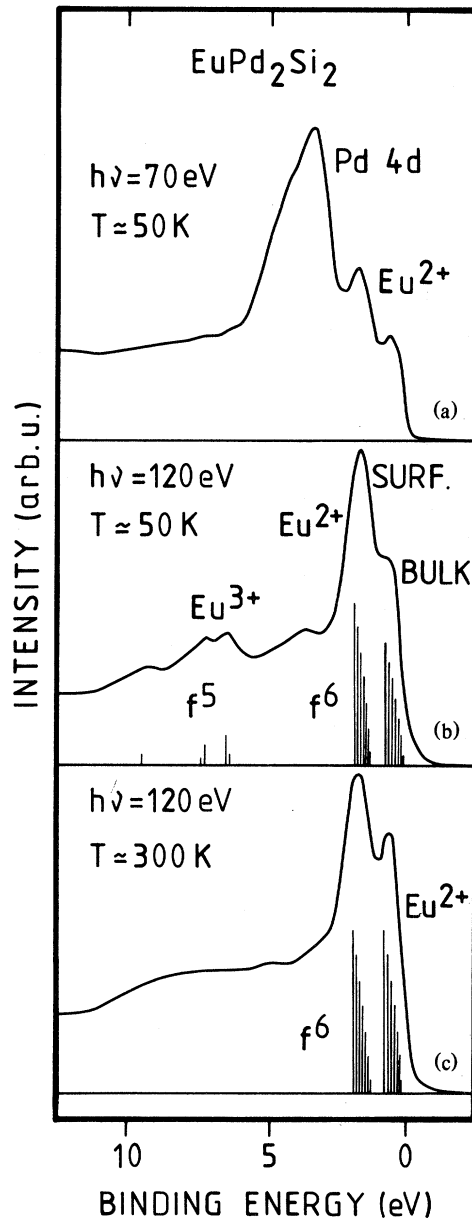


FIG. 1. Angle-integrated energy-distribution curves of photoelectrons emitted from EuPd_2Si_2 at (a) $h\nu = 70$ eV and $T = 50$ K, (b) $h\nu = 120$ eV and $T = 50$ K, and (c) $h\nu = 120$ eV and $T = 300$ K.

the $f^6(5d6s)^3$ and $f^7(5d6s)^2$ states are energetically degenerate. The divalent portion of the spectrum is, however, dominated by a structure at 1.1–1.2-eV higher binding energy which we interpret as a surface-shifted Eu^{2+} emission. When the low-temperature phase is entered, the bulk divalent contribution is reduced and the characteristic trivalent multiplet pattern appears in the energy range 6–10 eV. The surface 4f emissions seems, however,

to be unaffected.

What information can be obtained from the relative intensities of the various 4f features? At $h\nu = 120$ eV the electron escape depth λ is ~ 6 Å,¹¹ while in EuPd_2Si_2 the Eu-Eu interlayer distance is ~ 5 Å. With these parameters we sample, to $\sim 55\%$, the top monolayer of Eu atoms, to $\sim 25\%$, the second monolayer, and to $\sim 20\%$, the remaining layers. Hence, in the simple picture where the top monolayer is in a surface-shifted divalent state and all the other atoms exhibit the bulk mixed valence, we would expect the intensity of the “bulk” Eu^{2+} feature to be nearly completely transferred to the Eu^{3+} feature at 50 K, where the bulk valence is 2.9. Clearly this is not the case, since at 50 K $\sim 20\%$ of the total 4f intensity is found in the Eu^{3+} feature and $\sim 35\%$ in the “bulk” Eu^{2+} feature. A possible explanation is that the second monolayer of Eu atoms is divalent at all temperatures and not measurably shifted from the deep-bulk Eu^{2+} emission. However, it is important to note that the second layer is not a well defined concept since we are not measuring a surface which has been well characterized topologically. Depending on how the EuPd_2Si_2 crystal actually fractures, the second Eu layer referred to above might consist of Eu atoms in certain cleavage planes where they are not surface atoms, but where they are still the topmost Eu atoms, being covered by a 2–4-Å-thick layer of Pd and Si atoms. While we find this to be the most reasonable interpretation of the observed “second layer,” we concede that uncertainties in our estimated intensities, the applied value of λ , and the surface topology render as speculative any of our attempted descriptions of the second layer.¹²

In Eu metal a surface shift in the Eu^{2+} emission of 0.6 eV has been observed,^{13,14} whereas it appears to be 1.1–1.2 eV in EuPd_2Si_2 . We shall attempt to explain this difference with arguments which focus on possible differences in the nature of the bonding between Eu metal and EuPd_2Si_2 . Recently, it has been shown¹⁵ how the metallic influence on core-level binding energies can be calculated within a scheme where the metallic screening of the photoionized hole state is explicitly taken into account. One term ΔE_{coh} , which enters into this scheme, described how the bonding properties (hence *cohesion*) of the ionized site changes due to the photoemission of a core electron in the presence of the concomitant metallic screening within the valence shell. If the screening takes place in a bonding orbital, this increases the cohesive energy, corresponding to $\Delta E_{\text{coh}} > 0$; conversely, if the screening takes place in an antibonding orbital, $\Delta E_{\text{coh}} < 0$.

In the case of a surface atom we must consider the fact that it has an incomplete coordination. Due to the broken bonds, ΔE_{coh} will therefore be reduced at the surface.^{15,16} If we write $\Delta E_{\text{coh}}^{\text{surf}} = \alpha \Delta E_{\text{coh}}^{\text{bulk}}$, then the surface shift will be $(1 - \alpha)\Delta E_{\text{coh}}^{\text{bulk}}$. In Ref. 15,

the estimate $\alpha = 0.8$ was used, based on earlier empirical studies. Thus, in Eu metal, $\Delta E_{\text{coh}}^{\text{bulk}} = 2.4$ eV (Ref. 17) gives a calculated surface shift of 0.5 eV towards higher binding energies, which agrees closely with the experimental result, 0.6 eV. Within this model chemical shifts in metallic compounds can also be described by changes in ΔE_{coh} .^{15,18} If the chemical shift is such that the magnitude of ΔE_{coh} increases, we expect also the surface shift to increase. In the compound EuPd_2Si_2 , the bulk 4*f* emission is shifted by 1.4 eV towards E_F (the direction of increasing ΔE_{coh}) relative to Eu metal; hence $\Delta E_{\text{coh}}^{\text{bulk}}$ (EuPd_2Si_2) = 3.8 eV. Since $\Delta E_{\text{coh}}^{\text{bulk}}$ (Eu metal) = 2.4 eV yields a *measured* surface shift of 0.6 eV, the corresponding surface shift expected for EuPd_2Si_2 is $(3.8/2.4)0.6 \approx 1.0$ eV, which is close to the measured value of 1.2 eV reported herein. In other words the surface shift in EuPd_2Si_2 relative to that in Eu metal can be well accounted for within this model. Better agreement would be fortuitous in view of the uncertainty in α and its dependence on crystal structure orientation¹⁵ and, in the case of a compound, its dependence on the specific surface composition.

In summary, we have both identified and accurately measured the surface shift in a mixed-valent compound. The facility of being able to obtain spectra for widely different bulk valences (2.2+ at 300 K and 2.9+ at 50 K) has allowed us to more thoroughly characterize the nature of the surface state than oth-

erwise possible. Our conclusion is that the surface state of EuPd_2Si_2 is confined to the top one or two monolayers and it is divalent (rather than mixed valent) irrespective of the valence of the bulk. The relatively small change in the "bulk" divalent 4*f* emission when the valence is changed from 2.2 to 2.9 suggests that the mixed-valent bulk is not simply terminated by one divalent layer of Eu surface atoms. As one possibility, it is shown that with a reasonable value for the electron escape depth it is possible to reproduce the spectrum by assuming the existence of a "second layer" of Eu atoms which are in a stable valent, but (almost) unshifted, Eu^{2+} state. The fact that the surface shift of the Eu^{2+} emission (1.1–1.2 eV) is roughly twice that reported of Eu metal (0.6 eV) is reconcilable within the screening model discussed in Ref. 15, if one takes into account the measured differences in the bulk emission spectra of the two systems.

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¹G. K. Wertheim and G. Crecelius, *Phys. Rev. Lett.* **40**, 813 (1978).

²J. W. Allen, L. I. Johansson, I. Lindau, and S. B. Hagström, *Phys. Rev. B* **21**, 1335 (1980).

³W. Gudat, M. Campagna, R. Rosei, J. H. Weaver, W. Eberhardt, F. Hulliger, and F. Kaldis, *J. Appl. Phys.* **52**, 2123 (1981).

⁴G. K. Wertheim, W. Eib, E. Kaldis, and M. Campagna, *Phys. Rev. B* **22**, 6240 (1980).

⁵K. H. J. Buschow, M. Campagna, and G. K. Wertheim, *Solid State Commun.* **24**, 253 (1977). The spectra for YbAl_3 and EuCu_2Si_2 reported here, when considered in the light of more recent developments, suggest the presence of both bulk and surface divalent initial states. See also G. Kaindl, B. Reihl, D. E. Eastman, R. A. Pollak, N. Mårtensson, B. Barbara, T. Penney, and T. S. Plaskett, *Solid State Commun.* (in press).

⁶D. Rossi, R. Marazza, and R. Ferro, *J. Less Common Met.* **66**, 17 (1979).

⁷See, e.g., J. M. Lawrence, P. S. Riseborough, and R. D. Parks, *Rep. Prog. Phys.* **44**, 1 (1981).

⁸E. V. Sampathkumaran, R. Vijayaraghavan, K. V. Gopalakrishnan, R. G. Pillay, H. G. Devare, L. C. Gupta, B. Post, and R. D. Parks, in *Valence Fluctuations in Solids*, edited by

L. M. Falicov, W. Hanke, and M. B. Maple (North-Holland, Amsterdam, 1981), p. 193.

⁹D. E. Eastman, J. J. Donelon, N. C. Hien, and F. J. Himpsel, *Nucl. Instrum. Methods* **172**, 327 (1980).

¹⁰See, e.g., S. M. Goldberg, C. S. Fadley, and S. Kono, *J. Electron Spectrosc. Relat. Phenom.* **21**, 285 (1981).

¹¹See, e.g., B. Feuerbacher and R. F. Willis, *J. Phys. C* **9**, 169 (1976).

¹²Neither can we, in principle, exclude the possibility that the second layer is mixed valent, but with its effective valence reduced from the true bulk value of 2.9 to 2.3–2.4, while still exhibiting the same kind of temperature dependence as the deep bulk.

¹³L. I. Johansson, A. Flodström, S.-F. Hörnström, B. Johansson, J. Barth, and F. Gerken (unpublished).

¹⁴W. Schneider, N. Mårtensson, and B. Reihl (unpublished).

¹⁵B. Johansson and N. Mårtensson, *Phys. Rev. B* **21**, 4427 (1980).

¹⁶A. Rosengren and B. Johansson, *Phys. Rev.* **22**, 3706 (1980).

¹⁷This value for $\text{Eu} 4f^7$ is obtained by interpolating between the divalent metals $\text{Ba} 4f^0$ and $\text{Yb} 4f^{14}$, for which the same values as in Ref. 15 have been used.

¹⁸P. Steiner, S. Hüfner, N. Mårtensson, and B. Johansson, *Solid State Commun.* **37**, 73 (1981).