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### Authors

Frank, KH  
Reihl, B  
Fisk, Z  
[et al.](#)

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**BULK AND SURFACE VALENCE OF YbBe<sub>13</sub>\***

K. H. FRANK and B. REIHL

*IBM Zurich Research Laboratory, 8803 Rüschlikon (Switzerland)*

Z. FISK

*Los Alamos National Laboratory, Los Alamos, NM 87545 (U.S.A.)*

G. SCHMIESTER

*Institut für Atom- und Festkörperphysik, Freie Universität, D-1000 Berlin 33 (F.R.G.)*

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**Summary**

We report angle-integrated photoemission results on clean and oxidized YbBe<sub>13</sub> samples, at and below 300 K, which show YbBe<sub>13</sub> to have a trivalent bulk ( $\bar{v} = 2.9_{-0.02}^{+0.1}$ ) and a divalent surface layer. The bulk valence, independently derived from temperature-dependent L<sub>III</sub>-edge X-ray absorption measurements, is found to be three.

**1. Introduction**

The isostructural XBe<sub>13</sub> alloys (X ≡ rare earth or actinide element) form an interesting class of materials. For superconducting UBe<sub>13</sub> [1] and magnetic NpBe<sub>13</sub> [2], an anomalously high electronic specific-heat value has been reported ( $\gamma \sim 1 \text{ J mol}^{-1} \text{ K}^{-2}$ ) which classifies these materials as heavy-fermion systems. On the other hand, CeBe<sub>13</sub> provides evidence of a configurational instability of the Ce 4f shell [3, 4]. The subject of this paper, YbBe<sub>13</sub>, has been found to order antiferromagnetically below  $T_N \approx 1.3 \text{ K}$  [5], but above  $T_N$  it shows an anomalously large linewidth in inelastic magnetic neutron scattering, which may indicate that the Yb ions are also near a valence instability [6]. The latter could also be inferred from Mössbauer measurements for the paramagnetic state [7]. The lack of volume dependence of resistivity features suggests, however, that YbBe<sub>13</sub> is not mixed-valent in the ground state, but above  $T_N$  resistive anomalies exist, possibly owing to "Kondo-sideband" scattering [8]. Here, we apply bulk-sensitive L<sub>III</sub>-edge X-ray absorption and photoemission spectroscopy at

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$h\nu = 40.8$  eV (*i.e.*, bulk and surface sensitive) to  $\text{YbBe}_{13}$ . We find an essentially trivalent bulk with a divalent surface layer, as was previously found, for example, for Sm [9],  $\text{EuPd}_3$  [10] and  $\text{TmS}$  [11]. Divalent surface layers are generally present on all promotional-type mixed-valent systems, *e.g.*,  $\text{TmSe}$  [11],  $\text{Sm}_x\text{Y}_{1-x}\text{S}$  [12], and  $\text{Yb}_x\text{Y}_{1-x}\text{Al}_2$  [13].

## 2. Experimental details

Flux-grown single crystals of  $\text{YbBe}_{13}$  [8] were fractured under a vacuum of  $p < 1 \times 10^{-10}$  Torr and immediately irradiated with He(II) ( $h\nu = 40.8$  eV) radiation from a helium discharge lamp (Leybold-Heraeus) in a system originally designed for inverse photoemission [14]. Photoemission energy-distribution curves (EDCs) were taken within 2 min using a  $180^\circ$  hemispherical energy analyzer (Leybold-Heraeus). The overall resolution (electrons and photons) was 0.2 eV. The sample could be cleaved at room temperature as well as at 100 K.

For the X-ray absorption measurement, a sample previously used for photoemission was finely powdered under a dry argon atmosphere and pressed into paraffin wax. The intensities of the incident and transmitted X-rays were monitored as a function of energy using tunable synchrotron radiation from the EXAFS-II spectrometer at the HASYLAB, DESY, Hamburg [15]. Near the Yb-L<sub>III</sub> edge, around 8.9 keV, the energy resolution was 2 eV. Data were taken at 300 K and 5 K.

## 3. Results and Discussion

In Fig. 1(a) we present a photoemission EDC of clean  $\text{YbBe}_{13}$  fractured at room temperature. We note the  $\text{Yb}^{2+}$  ( $4f^{13}$ ) doublet near the Fermi level  $E_F = 0$ . The  $\text{Yb}^{3+}$  ( $4f^{12}$ ) multiplet can be recognized in the binding-energy range 5 - 11 eV similar to that in mixed-valent  $\text{YbAl}_2$  [13]. For clarity, in Fig. 1(a) we have included the bar diagram representing the  $4f^{13}$  final-state multiplet taken from  $\text{Tm}^{2+}$  [11] with an increase of the splittings by 10% owing to the additional nuclear charge in Yb. As becomes clear from the EDC in Fig. 1(a), the  $\text{Yb}^{3+}$  multiplet peaks rest on a broad emission feature with a maximum around 7 eV. By comparison with a He(I) ( $h\nu = 21.2$  eV) EDC (not shown), we attribute this broad emission to s,p states of Be similar to those in  $\text{UBe}_{13}$  [16]. There have been discussions as to whether oxygen 2p emission could be the origin of this feature [17, 18]. To check this, we have exposed clean  $\text{YbBe}_{13}$  to 0.75 L  $\text{O}_2$  (1 L = 1 Langmuir =  $10^{-6}$  Torr  $\times$  1 s), Fig. 1(b). The changes are dramatic. The  $\text{Yb}^{3+}$  emission is completely suppressed by the huge increase in the O 2p emission (note the factor, 2, in Fig. 1(a) relative to Fig. 1(b)), indicating the high sensitivity of the surface to  $\text{O}_2$ . This leads us to believe that the freshly-fractured surface is oxygen-free. In fact, further exposure of  $\text{O}_2$  increased the O 2p emission as can be

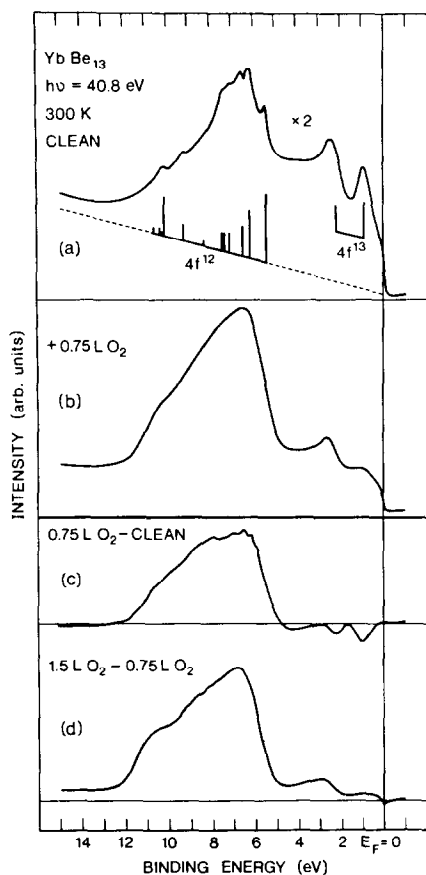


Fig. 1. Angle-integrated photoemission EDCs at  $h\nu = 40.8$  eV for (a) clean  $\text{YbBe}_{13}$ ; (b) plus 0.75 L  $\text{O}_2$ . Difference curves; (c) "0.75 L  $\text{O}_2$ " minus "clean"; (d) "1.5 L  $\text{O}_2$ " minus "0.75 L  $\text{O}_2$ ".

seen from the difference spectra in Figs. 1(c) and 1(d). The saturation level was only reached after 10 L  $\text{O}_2$ .

As an additional check, we fractured  $\text{YbBe}_{13}$  at 100 K to avoid oxygen diffusion from the bulk [18]. Again, we found an EDC similar to the one in Fig. 1(a), in particular the trivalent Yb multiplet resting on top of the broad Be s,p emission. The difference between cold and warm-fractured  $\text{YbBe}_{13}$  is an  $\sim 20\%$  reduced intensity of the  $\text{Yb}^{2+}$  doublet near  $E_F$ . This may indicate some Yb atoms segregating to the surface at room temperature. Upon oxidation, Yb forms trivalent  $\text{Yb}_2\text{O}_3$ , but the multiplet structure is completely smeared out by the O 2p emission [19]. The fact that we can clearly discern the  $f^{12}$  peaks in fig. 1(a) is another indication that the fractured  $\text{YbBe}_{13}$  surfaces are clean and that the underlying broad s,p emission is Be-derived.

We now turn to the  $\text{Yb}^{2+}$  ( $4f^{13}$ ) doublet near the Fermi level. It is interesting to find the  ${}^2F_{7/2}$  component at 0.9 eV and a shoulder cut by  $E_F$ . For a homogeneously mixed-valent system, the bulk divalent component has

to be pinned at  $E_F$ , if screening effects are neglected [13]. On the other hand, it has now been established that all mixed-valent systems (with the exception of Ce systems) have a divalent surface layer, *e.g.*,  $\text{EuPd}_2\text{Si}_2$  [10],  $\text{TmSe}$  [11],  $\text{Sm}_x\text{Y}_{1-x}\text{S}$  [12], and  $\text{Yb}_x\text{Y}_{1-x}\text{Al}_2$  [13]. Even some trivalent systems such as  $\text{Sm}$  [9],  $\text{EuPd}_3$  [10] and  $\text{TmS}$  [11] exhibit a divalent surface layer. From the non-zero binding energy of the intense  $f^{13}$  doublet in Fig. 1(a), we can immediately conclude that  $\text{YbBe}_{13}$  has a divalent surface layer. The 0.9 eV position of the surface  $^2F_{7/2}$  component is close to the value found for  $\text{Yb}_x\text{Y}_{1-x}\text{Al}_2$  [13], which is around 1.1 eV. By contrast, elemental Yb metal exhibits the  $^2F_{7/2}$  surface component at 1.7 eV binding energy [20].

The question now arises, whether a bulk  $4f^{13}$  doublet with low spectral intensity could cause the shoulder near  $E_F$  in Fig. 1(a), as would be expected for a nearly trivalent ( $\bar{v} < 3$ ) system. We have therefore tried to fit the experimental spectrum in the range 0 - 4.5 eV with two sets of Lorentzian broadened  $f^{13}$  doublets (ratio of the 5/2 - 7/2 component 0.75; spin-orbit splitting 1.27 eV [13]) for the bulk and the surface. Although, in principle, the EDC could be fitted by a single surface doublet, owing to the ambiguity in subtracting the underlying Be emission near  $E_F$ , 10% of the divalent spectral intensity could stem from a  $\text{Yb}^{2+}$  bulk doublet. Hence, the lower limit for the bulk mean valence amounts to  $\bar{v} = 2.9_{-0.1}^{+0.1}$ . An independent experimental check could involve quenching of the surface emission by oxygen exposure, which would leave a possibly existent divalent bulk  $f^{13}$  emission unaffected. While it is known that this works quite well with rare-earth NaCl compounds [11, 12], intermetallic alloys such as  $\text{YbAl}_2$  [13] do not clearly show this effect, probably because of the simultaneous oxygen reaction of the non-rare-earth constituents in the alloy.

For  $\text{YbBe}_{13}$ , we have studied the behavior of the surface  $4f^{13}$  emission with  $\text{O}_2$  exposure in Figs. 1(b) - (d). The first 3/4 L  $\text{O}_2$  clearly reduces the divalent surface emission, as is clear from the difference spectrum of Fig. 1(c). The remaining emission, however, is still not pinned at  $E_F$  in Fig. 1(b), pointing to the non-existence of a bulk  $\text{Yb}^{2+}$  signal. Further  $\text{O}_2$  exposure results in an increase of the spectral intensity in the 0 - 4 eV range (see the difference curve of Fig. 1(d)), which saturates after 10 L  $\text{O}_2$ . This complex behavior cannot be used to clarify the question of a small  $\text{Yb}^{2+}$  signal hidden in the intense  $\text{Yb}^{2+}$  surface emission of Fig. 1(a).

To obtain a definitive answer, we measured the X-ray absorption at the Yb  $L_{\text{III}}$  edge at 8.934 keV. This technique is bulk sensitive only. Our results are displayed in Fig. 2. The experimental curve measured at 5 K is identical to a spectrum of  $\text{YbBe}_{13}$  at 300 K. This is in contrast to  $\text{YbPd}_2\text{Si}_2$  with a temperature-dependent mean-valence which varies from  $\bar{v} = 2.9$  at 300 K to 2.8 at 16 K [15]. A fit to the  $L_{\text{III}}$ -edge profile performed in the same way as for  $\text{YbPd}_2\text{Si}_2$  finally revealed that no divalent Yb is present in bulk  $\text{YbBe}_{13}$ , as the photoemission results could only suggest (see the discussion above).

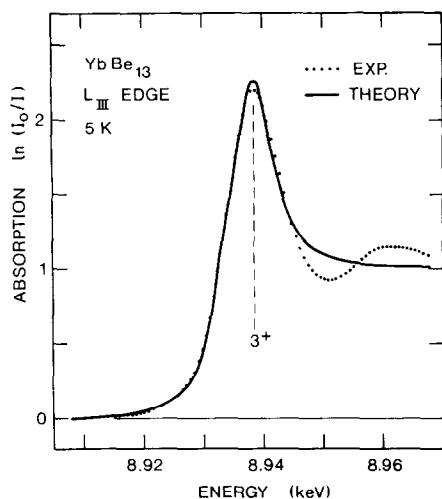


Fig. 2. Yb  $L_{III}$ -edge X-ray absorption of  $YbBe_{13}$ . The dotted line represents the experiment at a sample temperature of 5 K and is identical to a spectrum taken at 300 K. The solid line is a fit using a single  $Yb^{3+}$   $L_{III}$  edge. Deviations at higher energies are due to the EXAFS oscillations.

#### 4. Conclusion

From temperature-dependent  $L_{III}$ -edge measurements, we derive that  $YbBe_{13}$  is trivalent in the bulk. With photoemission spectroscopy, we find a trivalent bulk and a divalent surface layer. The Be s,p emission produces a broad emission feature centered around 7 eV.

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