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Title
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Permalink
https://escholarship.org/uc/item/1b3868kn

Journal
Physical Review B, 95(19)

ISSN
2469-9950

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Publication Date
2017-05-11

DOI
10.1103/PhysRevB.95.195126

Peer reviewed
Irreversible proliferation of magnetic moments at cleaved surfaces of the topological Kondo insulator SmB$_6$


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(Received 4 April 2017; published 11 May 2017)

The compound SmB$_6$ is the best established realization of a topological Kondo insulator, in which a topological insulator state is obtained through Kondo coherence. Recent studies have found evidence that the surface of SmB$_6$ hosts ferromagnetic domains, creating an intrinsic platform for unidirectional ballistic transport at the domain boundaries. Here, surface-sensitive x-ray absorption (XAS) and bulk-sensitive resonant inelastic x-ray scattering (RIXS) measurements have shown that the density of large-moment atomic multiplet states on a cleaved surface grows irreversibly over time, to a degree that likely exceeds a related change that has recently been observed in the surface $4f$ orbital occupation.

DOI: 10.1103/PhysRevB.95.195126

The topological Kondo insulator (TKI) state is a variant of the topological insulator state [1–4], in which a topologically ordered insulating electronic band structure is obtained from Kondo physics. The realization of a TKI state in mixed-valent SmB$_6$ was strongly indicated by early theoretical investigations [4,5], and has now been established through direct measurement of the topological surface states via angle resolved photoemission [6–11] and transport studies [12,13]. Strong evidence has recently been found suggesting that the surface of polished SmB$_6$ samples can also host ferromagnetic domains [13], a property that is theoretically associated with exotic axion electrodynamics, an inverse spin-galvanic effect, and ballistic one dimensional transport channels at domain boundaries [14–16]. Moreover, surface sensitive x-ray photoemission (XPS) measurements have shown that the surface $4f$ occupation evolves irreversibly towards $4f^5$ as a function of time following cleavage in ultrahigh vacuum (UHV) [17]. Here, multiplet-dominated x-ray absorption spectroscopy (XAS) and resonant inelastic x-ray scattering (RIXS) measurements in the vacuum ultraviolet (VUV) regime are used as a symmetry-sensitive probe to map the Sm N$_{4,5}$-edge excitations and show that a similarly large change in the density of large-moment samarium sites accompanies this time evolution. This evolution is consistent with expectations for the transition from a Kondo insulating state to magnetism, and represents a means for incrementally tuning the strength of the surface magnetic instability.

Measurements were performed at the beamline 4.0.3 (MERLIN) RIXS endstation (MERIXS) [18,19] at the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory. Large single crystals of SmB$_6$ were grown by the Al flux method as in Ref. [17], cleaved at low temperature, and maintained at a UHV pressure of approximately $3 \times 10^{-10}$ Torr. The photon beam had a grazing $30^\circ$ or angle of incidence to the cleaved [001] sample face, and scattered photons were measured at $90^\circ$ to the incident beam trajectory. XAS was measured using the total electron yield (TEY) method, and the expected penetration depth of measurements is roughly $d \lesssim 2$ nm for XAS [20] and $d \sim 10–30$ nm for RIXS [21]. To minimize sensitivity to surface inhomogeneity, the beam profile on the sample was configured as a very broad strip with dimensions of roughly $10 \times 600 \mu$m$^2$ (similar results from additional cleaves are shown in the online Supplemental Material (SM) [22]).

Atomic multiplet simulations were performed with typical renormalization values for the multipolar Slater-Condon interaction parameters [22]. Similar multiplet models that focus on Sm $f$ electrons, disregarding the itinerant $5d$ electron gas, have been remarkably successful in reproducing XAS and XPS features of SmB$_6$ [11,23]. The multiplet ground states have $f$-electron angular momentum quantum numbers of $(4f^5) J = 5/2$ and $(4f^6) J = 0$, representing the presence or absence of a hole in the $J = 5/2$ $4f$ bands. The atomic multiplet picture is expected to be most accurate as a description of the resonance states, which are dominated by extremely strong angular momentum coupling between the $4d$ core hole and $5d$ electrons on the scattering site ($a \sim 20$ eV combined energy scale). Multiplet state energetics in the VUV are defined in terms of coherent local moment symmetries. In contrast to the previous study of $4f$ charge density at the SmB$_6$ surface [17], atomic multiplet measurements in the VUV are sensitive to the coherent multiparticle symmetry of electrons in hybridized electronic orbits involving both the scattering site and neighboring atoms [24,25]. This multiplet symmetry can be thought of as the “nominal valence” state defining local moment degrees of freedom, and can deviate significantly from the atomically resolved charge density.

The samarium N$_{4,5}$-edge XAS spectrum of a pristine SmB$_6$ surface that has been recently cleaved and maintained at $T < 100$ K within UHV is shown in Fig. 1(a) (blue curve). To facilitate comparison of features, the nonresonant background has been aligned beneath the resonance at $h\nu = 123$ eV, and the curves have been set to have the same integrated area. The
Aged. Difference spectra in Fig. 1(b) show that, as time progresses, spectral intensity shifts into higher energy features at $h\nu > 136$ eV, and the sharper 126–133 eV features shift into a new spectral pattern that bears little resemblance to that seen initially. Even though the time interval between each pair of successive curves is approximately the same (45 to 60 min), the magnitude of the change is significantly larger for the interval from 4.5 to 5.5 h, in which the sample was heated to room temperature. Cycling back to low temperature (black curve) resulted in only small quantitative changes. Later scans did not reveal continued changes; however, the aging trend can be taken further still by exposing the sample surface to air (see red curve), suggesting that aging the surface is promoting changes in the $f$-electron count that resemble oxidation. The fractional change in feature intensities after thermal cycling is dramatic, and ranges from 10% to 50% throughout most of the spectrum.

To identify the physical significance of the surface evolution, a multiplet simulation in Fig. 1(c) shows the features expected in Sm$_{1.5}$-edge XAS from $J = 0$ and $J = 5/2$ sites. Dashed drop lines highlight an excellent qualitative match between the regions that lose intensity during the aging process and the $J = 0$ features, while the $J = 5/2$ features correlate with a gain (or reduced loss) of intensity. Only one feature is clearly anomalous in this analysis. The lowest energy XAS peak at $h\nu = 126.6$ eV is not reproduced by either the $J = 0$ or the $J = 5/2$ multiplet calculation, and has temperature dependence consistent with a $J = 5/2$ symmetry attribution.

Similar XAS measurements have also been performed as a function of time on an electron doped sample with the composition Sm$_{0.7}$La$_{0.2}$B$_6$ (see Fig. 2). In this case, the sample was maintained at $T < 100$ K for a much longer 46 h period, and the measurements confirm earlier observations that the aging process at low temperature proceeds on a time scale longer than 1 day [17]. Heating to $T = 250$ K produced small changes that were fully reversed upon cycling back to $T < 100$ K. This is in contrast to the more rapid measurement on undoped SmB$_6$, and suggests that the physical end point of low temperature aging is the same as the rapidly achieved end point of room temperature aging.

Lanthanum is expected to act as a net electron donor, entering an ionization state much closer to $3+$ as compared to Sm. Doping into the Sm 4$f$ orbitals of roughly $0.3e^-$/La atom is attributed from susceptibility studies [31]. The initial Sm$_{0.7}$La$_{0.2}$B$_6$ XAS spectrum is nearly identical to the slightly aged $t = 4.5$ h spectrum of undoped SmB$_6$, and the final aged (cycled) curve is qualitatively identical to XAS from the fully aged undoped SmB$_6$ sample. The fact that $J = 5/2$ features in the base ($t \sim 3$ h) spectrum of Sm$_{0.7}$La$_{0.2}$B$_6$ are more prominent than in the low temperature spectrum of SmB$_6$ is at odds with the identification of La as an electron donor, and suggests some variability in the nature of the cleaved surface (this is confirmed in Fig. S3 of the SM [22]).

Measuring resonant inelastic scattering at the photon energies used for XAS reveals a wide range of excitations, some of which are quite sharp in energy, as seen in Fig. 3(a). Prominent features at $E = 0.9$, 2.5, 3.7, and 5.2 eV appear to be Raman-like (nondispersive); however, the upper bound of intensity on the energy loss axis disperses with a slope similar to 1 as a function of incident energy, starting from $\sim 3$ eV at an incident energy of $h\nu = 126.6$ eV, as expected for scattering scenarios that involve interplay with degrees of freedom that have similar energetics with or without a core hole present. This suggests that a truly accurate model spectrum contains a large number of features, and the higher energy features have broader line shapes, as is the typical trend for core hole lifetimes at a multiplet-split resonance [24–30]. Relatively sharp line shapes are observed in the incident energy range from 126 to 133, suggesting that there may be a charge transfer threshold at $h\nu \sim 133$ eV [25,26].

The spectrum changes pronouncedly as the sample is aged. Difference spectra in Fig. 1(b) show that, as time progresses, spectral intensity shifts into higher energy features at $h\nu > 136$ eV, and the sharper 126–133 eV features shift into
regions with large intensity in the can attribute a tentative correspondence between energy loss intensity seen by RIXS [see highlighted regions in Figs. 3(a) and 3(b)]. One relatively localized excitations, and to yield accurate matrix multiplet model is still expected to be accurate for certain onset of a large density of itinerant continuum states; of the RIXS excitations must incorporate significant nonlocal physics, going beyond the degrees of freedom on a single scattering site. The RIXS spectrum and optical conductivity [32–34] both pick up intensity from roughly 1.5 eV, suggesting the onset of a large density of itinerant continuum states; however, the optical data contain no candidates for any of the energetically sharp features seen by RIXS.

In spite of not fulfilling this requirement, the atomic multiplet model is still expected to be accurate for certain relatively localized excitations, and to yield accurate matrix elements of the “direct RIXS” scattering process [27,35]. One can attribute a tentative correspondence between energy loss regions with large intensity in the J = 5/2 simulation and the intensity seen by RIXS [see highlighted regions in Figs. 3(a) and 3(b)]. The feature at E \sim 0.9 eV gives a particularly close correspondence, and has no competing interpretation within the J = 0 simulation [Fig. 3(c)]. This E \sim 0.9 eV mode is actually a collection of closely spaced features, with additional peaks visible in the h\nu = 127.8 and 130.8 eV curves. Lower energy excitations visible in the simulations are not resolved from the elastic line, which is strong due to the broad off-angle tail of specular reflection in the VUV [24]. The lack of easily identifiable J = 0 derived features may indicate that single-atom excitations on 4f^5 sites are shorter lived (i.e., broader), possibly because they can easily delocalize into 4f^6X states, where “X” indicates an electron that has entered a more delocalized band symmetry. The anomalous h\nu = 126.6 eV resonance, which does not occur in our multiplet simulations, resonates primarily with the 0.9 eV feature, corroborating identification of the h\nu = 126.6 eV resonance with scattering from a J = 5/2 site.

A sufficiently large increase in the density of J = 5/2 sites in the mixed-valent samarium lattice is expected to destabilize the Kondo insulating state and induce magnetism, as has been seen in high pressure studies [36–38]. The amplitude of the surface change can be evaluated from the XAS data in Fig. 1, if we adopt the approximation that the spectra can be broken down into linear combinations of pure J = 5/2 and J = 0 curves (see derivations in the SM [22]). The accuracy of this approximation is supported in the present case by the observation of a fairly stable isospectral (constant intensity) point at 136.7–137eV for all warming curves.

Monovalent J = 5/2 and J = 0 XAS spectra algebraically obtained from comparing SmB_6 XAS measurements at the pristine (t = 3 h) and aged (cycled) surface are plotted in Fig. 4(b). Shaded regions represent error margins as described in the caption, and are associated with different extrapolated changes in the population of J = 5/2 and J = 0 sites over the aging period. The outer shaded boundaries represent extreme scenarios that lead to clear anomalies in the extrapolated monovalent curves, such as duplicated features and negative XAS intensity [22]. The best fit J = 0 XAS curve is obtained with the assumption that the J = 5/2 population grows by a remarkable 60%–80%. Growth estimates beneath 40% lead to multiple significant artifacts in the extrapolated XAS spectrum. Based on the extrapolated XAS curves, we can assess that a single-atom multiplet calculation provides many matrix elements of the N_{4,5}-edge resonance process, but is of marginal use for understanding the RIXS excitations, and omits XAS features that appear to be associated with coupling to itinerant states.

High pressure studies have found that a new magnetic ground state [36–38] is realized in bulk SmB_6 beyond a crossover point thought to occur when the fractional density of 4f/5 sites reaches roughly n_{5/2} \sim 0.65 [37,38]. Combined examination of the extrapolated J = 5/2 and J = 0 curves enables an algebraic derivation of the J = 3 h J = 5/2 site density as n_{5/2} = 0.39 \pm 0.05 [22], with a surface evolution plotted in Fig. 4(a). In distinguishing n_{5/2} from the nominal bulk 4f occupancy, which is thought to be n_f \lesssim 5.5 [11,37–40], this picture suggests that the transition is one from a singlet-dominated low temperature regime, with fewer observed large-moment sites than the J = 4f occupancy alone would suggest, to an aged surface in which local moments are less screened. This scenario matches the attributed behavior...
as the crystal is driven into a magnetic state under pressure [37,38]. We note that the nature of this magnetic order achieved under pressure is not definitively understood; however, a proximate ferromagnetic state can be achieved from 1% Fe doping at ambient pressure [41]. The air-exposed end point of \( n_{5/2} \sim 0.9 \) is consistent with the proposed interpretation of an earlier soft x-ray \( M \)-edge XAS measurement [42].

A comprehensive interpretation of the mechanism behind the observed irreversible surface changes is beyond the scope of the present study. Such a theory may need to address multiple factors including the correlated electronic structure, the intrinsically polar and anisotropic nature of cleaved surfaces, and the presence of multiple known surface reconstructions [11,43,44]. The bulk of the sample also evolves towards a lower \( 4f \) occupancy with increasing temperature [9,11,37,39,40]. However, the bulk-sensitive RIXS spectrum undergoes no easily visible changes as a function of temperature [22], suggesting that surface aging is a far more dramatic effect. The La doped sample is thought to have roughly identical bulk temperature dependence [31].

These resonant x-ray absorption results show that the density of large-moment Sm sites in the top \( \lesssim 2 \) nm of cleaved SmB\(_6\) more than doubles as the surface ages in UHV. The increase can be accelerated by heating to room temperature, and is taken further through exposure to air. Lower energy excitations of SmB\(_6\) are mapped with RIXS, providing a window into dynamics and energetics of the valence electrons, which will serve as a reference for future theoretical and spectroscopic investigations. The large surface changes seen by electron yield XAS are distinct from the lack of extraordinary temperature dependence at depths of 10–30 nm, as evaluated from RIXS spectra. The increased density of large-moment sites on aged samples provides a plausible explanation for the recent observation of ferromagnetic domains at a polished SmB\(_6\) surface [13]. More generally, the apparent sensitivity of the surface evolution to temperature and the gas environment provides mechanisms for control of the surface properties, to achieve a desired interplay between surface magnetic moments and the topologically ordered bulk electronic structure.

The Advanced Light Source is supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. C.-H.M. was supported by the DFG (through SFB 1170 “ToCoTronics”, Project No. C06). We are grateful for productive discussions with H. Dehghani and J. Hoffman.
[22] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevB.95.195126 for technical notes pertaining to the measurements and the derivation of curves in Fig. 4.
[34] A. Tytarenko, Nakatsukasa, Y. K. Huang, S. Johnston, and E. van Heumen, From bad metal to Kondo insulator: temperature


Supplemental Material for: Irreversible proliferation of magnetic moments at cleaved surfaces of topological Kondo insulator SmB$_6$


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(Dated: April 20, 2017)
FIG. S1: **Multiplet and extrapolated monovalent XAS spectra.** (a) Numerical simulations of magnetically inert J=0 (4f⁰) sites and J=5/2 (4f⁵) moments. (b) Pure J=5/2 and J=0 XAS curves obtained from the procedure described below. Shaded regions indicate variability based on (darker) ±10% and (lighter) ±40% differences in the estimation of population change over the thermal aging cycle measured in Fig. 1 of the main text. Anomalous off-valence features are highlighted with red and blue dots.

**MODELING PARAMETERS**

The atomic multiplet simulation was performed with 4f-4f Slater-Condon terms were set to 75% of bare Hartree-Fock values, and core hole 4d-4f parameters set to 62% of Hartree-Fock values. Spin orbit coupling of core 4d and valence 4f electrons is set to Hartree-Fock values, and a perturbative crystal field composed of on-axis delta function potentials was used to impose the cubic lattice symmetry (corresponding to 10Dq=-0.02eV for a d-orbital basis). The core hole inverse lifetime is set to Γ=0.35 eV beneath $h\nu = 132.5$ eV, Γ=2.5 eV above $h\nu = 132.5$ eV, and Γ=4 eV for the highest energy resonance peak seen with each valence state (found at $h\nu \sim 140$ eV for J=0 and $h\nu \sim 148$ eV for J=5/2). Larger values at higher photon energies due to autoionization and intrinsic multiplet effects [1–6].
All scattering simulations are performed for the experimental polarization and scattering geometry. Simulated RIXS spectra are obtained using the Kramers-Heisenberg equation, with exactly diagonalized eigenstates of the model Hamiltonian (as in Ref. [7]).

**EXTRAPOLATION OF MONOVALENT XAS SPECTRA**

This section will discuss how the valence changes and monovalent J=0 and J=5/2 spectra have been identified, and the systematic error associated with the procedures applied. The site densities and monovalent XAS spectra are obtained as follows:

1. The first step in the analysis was to subtract a flat non-resonant background from the XAS spectra, and then normalize them to the sum of intensity from 125-150eV. These procedures are necessary so as to neglect irrelevant changes in the overall spectral intensity and non-resonant background caused by factors such as a difference in the degree of gas condensation from the vacuum at T=20K versus 300K.

2. Given a normalized set of XAS spectra, we adopt the assumption that the spectrum measured at each time ‘\(S(t)\)’ is a linear superposition of monovalent J=0 and J=5/2 spectra \(S_0\) and \(S_{5/2}\) (which must also be considered to be normalized - see further discussion below). This approximation is strongly justified by the correlation of features with monovalent calculations in Fig. 1-2 of the main text, and by the presence of a stable isospectral point at 136.7-137eV for all warming curves. The fraction of J=5/2 (0) intensity in the spectrum is referred to as \(r_{5/2}(t)\) \(r_0(t)\), and is related to the experimental spectra as \(S(t) = r_{5/2}(t)S_{5/2} + r_0(t)S_0\). The value \(r_{5/2}(t)\) is approximately equated with \(n_{5/2}(t)\), the fractional density of J=5/2 sites (see discussion of error below).

3. The difference spectrum \(D\) between the fresh and aged extremes is defined as \(D = S(5.5h) - S(3h)\). (Note that the t=5.5h sample XAS spectrum is measured after cycling to room temperature, and is thus highly aged.)

4. A guess is made for the change in the value of \(r_{5/2}(t)\) over the full time range, defined as \(g_{5/2} = \frac{r_{5/2}(5.5h) - r_{5/2}(3h)}{r_{5/2}(3h)}\). A corresponding monovalent J=0 XAS spectrum is algebraically obtained from this guess as \(S_0(g) = S(3h) - g_{5/2}^{-1}D\).
5. The J=0 spectrum $S_0(g)$ is evaluated as a function of different guess parameters ‘$g_{5/2}$’ to identify the reasonable range for values of $g_{5/2}$ (see Fig. S1(b)). Values that are too small result in negative XAS intensity, which is non-physical. Values that are too large or too small can also be identified by the appearance of J=5/2 features with positive or negative intensity, respectively. Artifacts of this sort are indicated with red dots in Fig. S1(b).

6. The same procedure is followed to identify $S_{5/2}$ and $g_0$. The absolute fractional intensity of the J=5/2 spectrum in individual temperature resolved XAS curves ($r_{5/2}(t)$) is uniquely determined from the combination of $g_0$ and $g_{5/2}$. In Fig. 4(a) of the main text, $r_{5/2}(t)$ is determined by optimizing the value of $r_{5/2}(3h)$ and using shaded regions to identify possible trends based on estimated error in the value of $g_{5/2}$. An additional horizontal error bar gives the estimated error in the starting value of $r_{5/2}(3h)$. The maximum likely value of $r_{5/2}(3h) \lesssim 0.45$ is confirmed by comparing with the XAS spectrum of an air-exposed sample, as described below.

Error sources and error bars related to this analysis have been evaluated as follows:

- **Accuracy of the evaluation criteria in step 5 above**: If we assume that the $h\nu = 148$ eV XAS feature is unique to J=5/2 sites, then error of $\lesssim \pm 0.1$ in the value of $g_{5/2}$ is easily achieved, represented by dark-shaded error margins in Fig. S1(b) and main paper trajectory graphs. The appearance of other artifacts such as from the $h\nu = 126.6$ and 140 eV J=5/2 features gives a hard lower constraint on the fractional change in $n_{5/2}$ over the temperature range, which is symmetrized to give the light-shaded error margins. The upper bound defined by this method is similar to the hard upper limit of $n_{5/2}(5.5h) = 1$

- **The approximation that J=0 and J=5/2 spectra have the same integrated intensity**: The relative integrated intensities of the J=0 and J=5/2 spectra are irretrievably lost as a consequence of the normalization described in step 1 above. The $n_{5/2}$ site density calculated by the method above actually represents the fraction of XAS intensity derived from a normalized J=5/2 spectrum. The N-edge 4f$^5$ multiplet ground state cross section is 12.5% larger than the 4f$^5$ cross section, and a larger 4f$^5$
total cross section will lead to an *overestimation* of the J=5/2 site density. For J=5/2 site densities measured here, the overestimation will be < 0.03, and is smaller than other sources of error in the analysis. The \( n_{5/2} \) values plotted in Fig. 4(a) of the main text have been shifted by 0.02 to account for this effect.

- **Accuracy of the determination of absolute fractional intensities in step 6 above**: The horizontal error bar in Fig. 4(b) of the main text show the maximum range of \( n_{5/2} \) values that can be obtained from values in the dark-shaded error margins for J=0 and J=5/2.

- **Stability of the TEY background**: Fano lineshapes and other irregularities in the non-resonant background should not create well formed spectral features, but may cause the absolute spectral intensity to be inaccurate in all XAS curves. These details are irrelevant to the algebra used to determine \( n_{5/2}(t) \), but call into question cases in which negative XAS intensity is used to establish boundary conditions in step 5 above.

- **An upper bound from the air-exposed sample**: An alternative estimate of the upper bound on the initial density of large moment sites can be established from the XAS spectrum of the air-exposed sample, by noting that \( r_{5/2}(\text{air}) \) cannot exceed 1. If the ratio \( g_{5/2} \) is held at the optimal estimated value, this upper bound is approximately \( r_{5/2}(3h)=0.45 \).

**BULK TEMPERATURE DEPENDENCE**

The temperature dependence of bulk-sensitive RIXS measurements is shown in Fig. S2. Changes in the 4f occupancy of roughly 10-20% over the 20→300K temperature range are attributed in the literature [8–11], however the signal to noise ratio and background intensity fluctuations in our RIXS data do not make this a very good criterium for associating RIXS features with different valence states. Most RIXS features appear to soften slightly in energy at higher temperatures, as expected due to lattice expansion and the thermalization of exchange energetics.
FIG. S2: Temperature dependence in RIXS. Vertically offset RIXS measurements performed at $h\nu = 132.2$ eV on a freshly cleaved sample maintained at low temperature. Curves were obtained over a period of several hours. An inset shows the incident photon energy on the extrapolated monovalent XAS spectra.

SURFACE INHOMOGENEITY

The cleaved surface of SmB$_6$ is known to be inhomogeneous on both nanometer and 100$\mu$m length scales [9, 12]. This is mitigated in our experiment by the large 600 $\mu$m width of the beam spot (in our slightly grazing measurement geometry). Similar XAS spectra were obtained from all low temperature measurements (see Fig. S3), however some measurements showed deviations that resembled mild aging. The amplitude of these differences was not seen to exceed 20% of the measured aging effect in Fig. 1. Due to the broad beam spot, it is possible that the variability is related to parts of the beam striking uncleaved (air exposed) sample regions in some measurements.

The beam height (z-axis width) was just $\sim 10$um, which means that thermal changes and cycling gave an effectively new beam spot, and rules out beam damage playing a dominant role in the aging mechanism. Scans as a function of z-axis beam position showed very similar XAS curves, when tested on nearby surface locations (within $\lesssim 100$um).

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FIG. S3: **Low-temperature spectra from 2 cleaved surfaces.** (thick black and red) XAS spectra of SmB$_2$ samples maintained at T=20K, measured 2-3 hours after cleavage. Thin curves show the difference between these spectra, scaled up by a factor of 5, and the difference spectrum between t=5.5h and 3h data from Fig. 1 in the main text.


