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## LETTER TO THE EDITOR

**Resonant photoemission from the 4d  $\rightarrow$   $\epsilon f$  shape resonance in Sb(0001)****Bongjin S Mun<sup>1,2,4</sup>, Guorong V Zhuang<sup>1</sup>, Philip N Ross<sup>1</sup>,  
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**Abstract**

The observation of resonant photoemission at shape resonance energy in Sb(0001) is reported. When the photon energy was tuned to the 4d  $\rightarrow$   $\epsilon f$  transition region of the Sb shape resonance ( $\sim 90$  eV), a Fano-like profile was observed in the photoelectron cross-section from the half-filled 5p valence orbitals. Two new, significant features appeared at photon energies above the 4d threshold: one in the gap between the filled 5s<sup>2</sup> and half-filled 5p bands, and the other at the Fermi level. The former is attributed to final state mixing in the autoionization decay of the  $\epsilon f$  transition state, and the latter to a two-photon photoionization process directly from the  $\epsilon f$  transition state.

Resonant photoemission (PE) spectroscopy is one of the new tools in condensed matter physics that has accompanied the development of synchrotron radiation sources [1, 2]. The method takes advantage of a variation in the photoionization cross-section of an atom when the photon energy is tuned across certain core-level excitation thresholds. The resonant PE process is frequently interpreted as a Fano resonance [3] caused by a coupling of the direct PE channel with an indirect PE channel opened by core excitation into an intermediate state [4]. In a Fano resonance [3], at energies closely above the excitation threshold, there is constructive interference between these channels leading to an increase in the photoionization cross-section, while just below threshold there is suppression of electron emission from destructive interference, producing a distinctive variation in the PE intensity as a function of photon energy. Mårtensson *et al* [5] have proposed that fitting the experimental PE intensity profile with the Fano lineshape is a convenient qualitative measure of the delocalization of the intermediate

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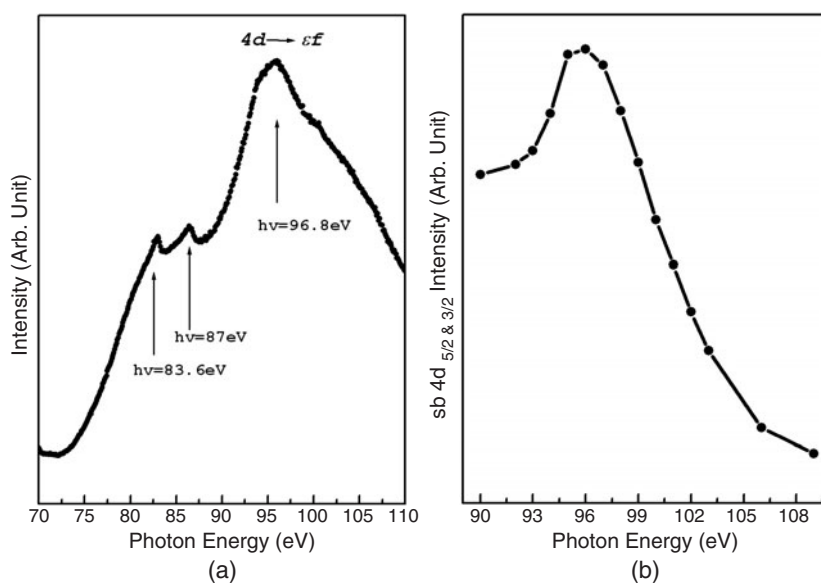
(core excited) state. In elements where the core excitation is a giant or shape resonance, the intermediate state has both delocalized states and a relatively long lifetime: two characteristics that should produce a distinct shape in the intensity profile of photoionization. We are aware of only a few studies of resonant photoemission of this type, all with rare-earth elements [6].

In the present letter, we show, for the first time, resonant valence band (VB) photoemission in the energy range of the  $4d \rightarrow \epsilon f$  shape resonance from the semi-metal Sb(0001). In the group V semi-metal Sb [7], there is little overlap between the valence and conduction bands. States near the Fermi level are highly localized and atomic in character; the ground state atomic configuration is  $5s^2 5p^3$ . In the Sb  $4d \rightarrow \epsilon f$  shape resonance, the maximum intensity in the x-ray absorption spectrum (XAS) appears at a much higher excitation energy than the nominal  $4d$  binding energy due to a high centrifugal potential barrier (several tens of electronvolts) that prevents the overlap of the  $\epsilon f$  wavefunctions with the  $4d$  wavefunction when the kinetic energy of the outgoing electron is small. These rather unique resonance features have been observed in a series of elements from Sn ( $Z = 50$ ) to Lu ( $Z = 71$ ), and many experimental and theoretical studies have been devoted to understanding the physics of this phenomenon [8–10]. We are aware of only one previous study of the shape resonance in Sb that was done by Brechignac *et al* [11], using Sb clusters containing from 4 to 36 atoms.

In this letter, we show that the  $4d$  x-ray absorption spectrum from an Sb(0001) crystal has the shape resonance seen in the photoionization spectra of Brechignac *et al* [11] for odd-numbered Sb clusters. The valence band spectra, on-and-off the shape resonance energies, produced variations in intensity, characteristic of interference, such as a Fano lineshape. In addition to the expected variations in intensity, characteristic of interference due to valence band spectra on and off the shape resonance energies, we identified on-resonance spectra that had a new feature near the Fermi level not typical of a Fano profile of intensity with photon energy.

The experimental measurements were carried out at the bending magnet beamline 9.3.2. of the Advanced Light Source at Lawrence Berkeley National Laboratory. The Sb(0001) sample was cleaved in air, then immediately introduced into the UHV chamber via a load-lock, and prepared with cycles of  $\text{Ar}^+$  bombardment and annealing for cleaning purposes. The long-range order of the sample surface was checked by LEED, and a sharp pattern with  $(1 \times 1)$  hexagonal symmetry was observed. An SES100 (Scienta) hemispherical electron analyser was used for the PE measurement. Under a pressure of less than  $2 \times 10^{-10}$  Torr, all PE spectra were taken at a direction normal to surface and photon incident angle of  $20^\circ$  from the sample surface. The total energy resolution was less than 0.2 eV. The plane of photon polarization the same as that of the electron analyser. Fluorescence detection was used for the measurement of x-ray absorption spectra (XAS) with a photon energy resolution of 0.1 eV.

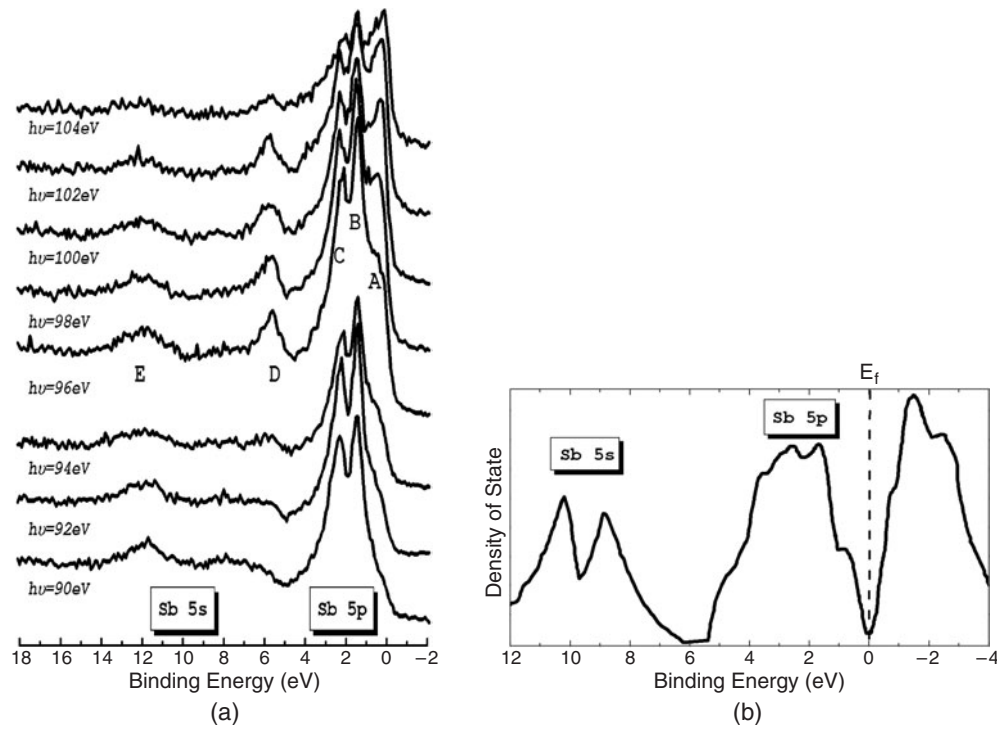
Figure 1(a) shows the absorption spectrum taken while the photon energy was scanned through the Sb  $4d \rightarrow \epsilon f$  shape resonance region. The overall shape and energy region of the spectrum is very similar to that reported by Brechignac *et al* [11] for Sb clusters with an odd number of atoms. As is clearly seen in the figure, the intensity of absorption reaches a maximum at  $\sim 96.8$  eV, about 64 eV above the Sb  $4d$  core level binding energy (i.e.  $\sim 32$  eV). However, in comparison to the photoionization results for Sb clusters [11], our absorption spectrum shows two distinctive peaks at photon energies near 83 and 87 eV. These features might have been also present in the photoionization data with Sb clusters, but the energy resolution and/or signal-to-noise ratio in those experiments was not sufficient to resolve these features. Although we do not know what causes these fine structure peaks at 83 and 87 eV, the presence of doubly excited state resonances can be expected in this energy region [12]. Enhancement of the photoionization cross-section, as photon energy scanning across the Sb  $4d \rightarrow \epsilon f$  shape resonance, should also be observed in the intensity of the Sb  $4d$  photoemission.



**Figure 1.** (a) X-ray absorption of Sb(0001) in total fluorescence yield mode obtained in the photon energy range of the Sb  $4d \rightarrow \epsilon f$  shape resonance. (b) The integrated intensity, obtained by integrating peaks of Sb  $4d_{5/2}$  and Sb  $4d_{3/2}$  of the Sb 4d photoemission (PE) peaks, is shown as a function of photon energy.

Such an intensity profile, as a function of photon energy, is shown in figure 1(b). As is shown clearly in figure 1(b), the profile of the Sb 4d PE intensity indeed follows that of the shape resonance in the XAS spectrum.

The normalized valence band PE spectra as a function of photon energy in the range from 90 to 110 eV are shown in figure 2(a). Due to the large acceptance angle of the analyser ( $\pm 5^\circ$ ) and the small momentum variation of the valence band photoelectrons ( $\Delta k = \sim 0.5$ ), these energy distribution curves (EDCs) should be regarded as total density of state (DOS) curves, i.e. without dispersion features from the band structure. The DOS has two main regions, the 5p region from 0 to 6 eV and the 5s region from 7 to 14 eV. The theoretical total DOS from the band structure calculation of Robertson [13] shown in figure 2(b) is in reasonable agreement with the experimental spectra (below  $h\nu = 96$  eV). However, for photon energies between 96 and 104 eV, new features appear, denoted by A and D, which are not part of the theoretical DOS, and thus are, by inference, from an indirect channel in the 4d excitation process. The distinct PE from the 5p states, denoted B and C in the figure, and the 5s band denoted E, show the expected enhancement in intensity as the photon energy is scanned through the shape resonance. To monitor the details of the resonant photoemission, the intensities of the features A–E, as a function of photon energy, are shown in figure 3. Interestingly, a Fano lineshape can be seen for the 5p and 5s states and the feature D appears in the 5s–5p gap, but not for the new feature A, very close to the Fermi level. As is well known, the Fano lineshape for the ionization cross-section arises from the interaction of the core hole with an energetically degenerate (resonant) continuum of states, leading to the quantum mechanical interference of the transition process [3, 4]. To our knowledge, no other resonant valence band photoemission at core level threshold shows such clear Fano lineshapes as those shown here for Sb(0001). The resonant photoemission from transition metals V, Cr, Mn and Co reported by Kaurila *et al* [14] showed intensity profiles to which the authors attributed a fractional contribution from an



**Figure 2.** The Sb(0001) valence band PE spectra (a), at photon excitation energies from 90 to 110 eV, are compared with theoretical total DOS (b) from the band structure calculation, indicating two main regions, the 5p region from 0 to 6 eV and the 5s region from 7 to 14 eV (see [14]).

‘atomic Fano resonance’. The closest resonant valence PE results to ours here for Sb are the results of Mårtensson *et al* [5] for Ni, who reported true Fano lineshapes, at photon energies near the  $L_3$  core level threshold, for both the normal valence states and the ‘satellite’ feature appearing at binding energy (BE)  $E_{BE}$  at 5.3 eV. More discussion will be given later regarding the Fano lineshapes of VB spectra. Because the 5s and 5p bands in Sb(0001) are well separated in energy and highly localized, there are three different final states, i.e. three different indirect channels, from autoionization of the  $4d^9 \epsilon f$  intermediate state:

(1) Direct channels:

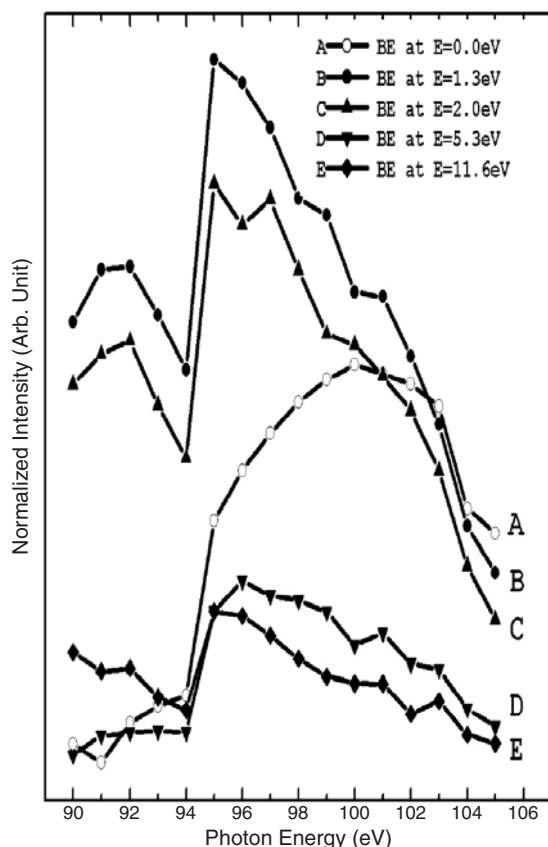
- (a)  $4d^{10}5s^25p^3 \rightarrow 4d^{10}5s^25p^2$  (p electron out),
- (b)  $4d^{10}5s^25p^3 \rightarrow 4d^{10}5s^15p^3$  (s electron out).

(2) Indirect channels:

- (c)  $4d^{10}5s^25p^3 \rightarrow 4d^95s^25p^3 \epsilon f \rightarrow 4d^{10}5s^25p^2$  (p electron out),
- (d)  $4d^{10}5s^25p^3 \rightarrow 4d^95s^25p^3 \epsilon f \rightarrow 4d^{10}5s^15p^3$  (s electron out),
- (e)  $4d^{10}5s^25p^3 \rightarrow 4d^95s^25p^3 \epsilon f \rightarrow 4d^{10}5s^{1.5}5p^{2.5}$  ( $|s\rangle + |p\rangle$  electron out).

State (e) is a hybridized sp final state producing photoemission in the energetic gap between the 5s and 5p bands. The interference between the direct and indirect channels produces three not two PE peaks, each having an intensity profile characteristic of a Fano resonance.

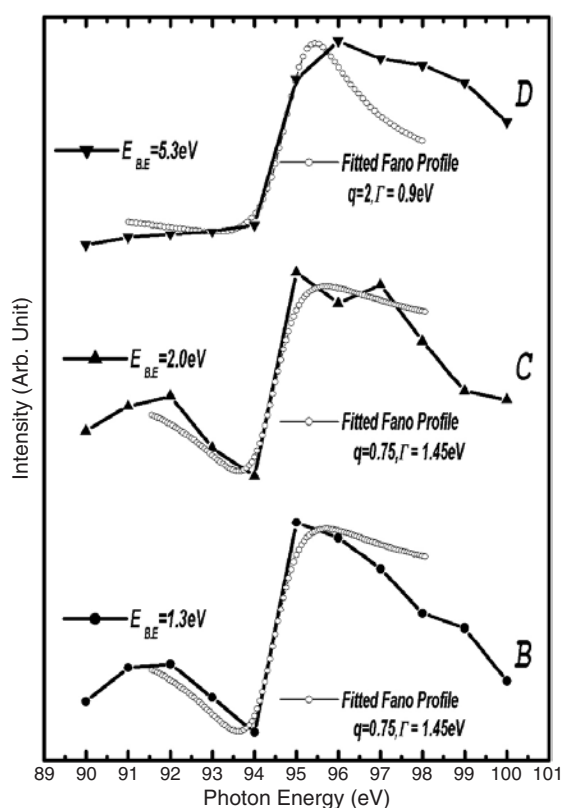
The physics behind the new feature A near the Fermi level has not, to our knowledge, been described before. A similar feature, the delay of the maximum position, having the same



**Figure 3.** The normalized resonant profile from the valence band spectra extracted from figure 2(a) at each position of binding energies: 0.0 eV (A), 1.3 eV (B); 2.0 eV (C), 5.3 eV (D) and 12.0 eV (E).

underlying physics, can also be seen in the shape resonant PE spectrum of La (metal) [15], although the authors of that paper did not comment on this feature. We suggest that this feature comes from a two-photon ionization process, where a second photon ionizes the  $4d^95s^25p^3 \epsilon f$  intermediate state before it decays. Since the effective 'binding energy' of the intermediate state is near zero, i.e. the centrifugal barrier having consumed all the kinetic energy from the first photon, the electron emitted by ionization by the second photon has a kinetic energy equal to the photon energy and thus it appears, on a binding energy scale, to be coming from the Fermi level of the sample.

It appears that profiles A and D show a trend different from those of B, C and E. To explore the observed behaviour, the resonant profiles in the valence band spectra at BE of 1.3 eV (B), 2.0 eV (C) and 5.3 eV (D) were fitted to a Fano profile. The standard expression of the Fano profile [4],  $I = (q + \epsilon)^2 / (\epsilon^2 + 1)$ , was applied to fit the experimental profile, where  $q$  is the Fano asymmetry parameter,  $\epsilon = (E - E_{th}) / \Gamma$  ( $E_{th}$  the resonance threshold energy, and  $\Gamma$  the lifetime width). The square of the Fano asymmetry parameter ( $q$ ) is proportional to the ratio between the transition probabilities of indirect autoionization process and that of direct photoemission continuum states over the core level width,  $\Gamma$ . As is shown in figure 4, the resonant profiles are not completely in agreement with the Fano profile. One of the main reasons for this difference is that the basic assumption of the Fano model starts from a discrete state and



**Figure 4.** The experimental resonant profiles at 1.3 eV (B), 2.0 eV (C), 5.3 eV (D) in figure 3 fitted to the theoretical Fano profile.

an underlying continuum state while this experimental system contains several discrete and several continuum states. However, the fitting result provides qualitative information on this particular resonance process. First of all, the trend of the fitting result shows a good agreement with the result of Mårtensson *et al* [5] in the Ni case. In the case of Sb(0001), the asymmetry parameter ( $q$ ) of the Fano profile of the intermediate state D is 2, while that of B and C from the VB spectra is 0.75. This finding, a lower  $q$  parameter of B and C at VB states and higher  $q$  parameter of D at an intermediate state, is consistent with what has been found in the Ni resonance case [5], which suggests that the D state is dominated by an indirect autoionization process. Second, the lifetime width ( $\Gamma$ ) of the Fano profiles of the intermediate state D is estimated to be 0.9 eV, narrower than that of 1.4 eV for the states B and C. The fact that the onset of the intermediate state D occurs simultaneously with that of state A, together with the narrower lifetime width of the intermediate state D, i.e. longer lifetime of intermediate state D, supports our previous assignment of feature A, near the Fermi level region in figure 3, as a two-photon photoionization process.

In this letter, we have reported the first resonant VB photoemission from the  $4d \rightarrow \varepsilon f$  shape resonance in Sb(0001). A Fano lineshape was found both at the 5s and 5p orbital states and its intermediate state (near  $\sim 5.3$  eV), suggesting an interference effect between the direct and indirect channels of this resonance process. Two significant new features appeared at photon energies above the 4d threshold, one in the gap between the filled  $5s^2$  and half-filled 5p bands, and the other at the Fermi level. The former is attributed to final state mixing in the

autoionization decay of the  $\varepsilon f$  transition state, and the latter to a two-photon photoionization process directly from the  $\varepsilon f$  transition state.

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