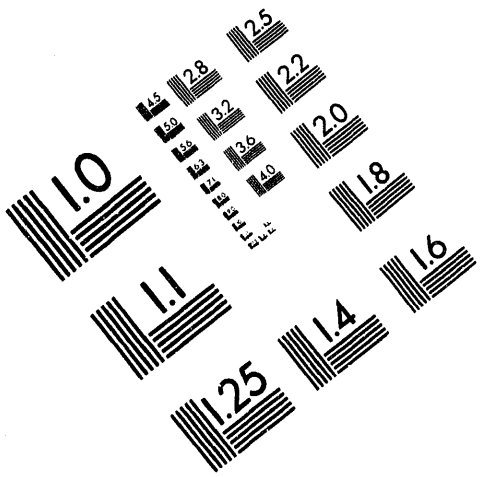

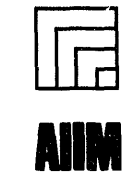

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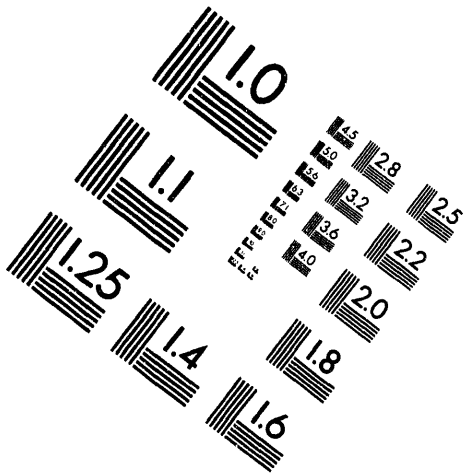

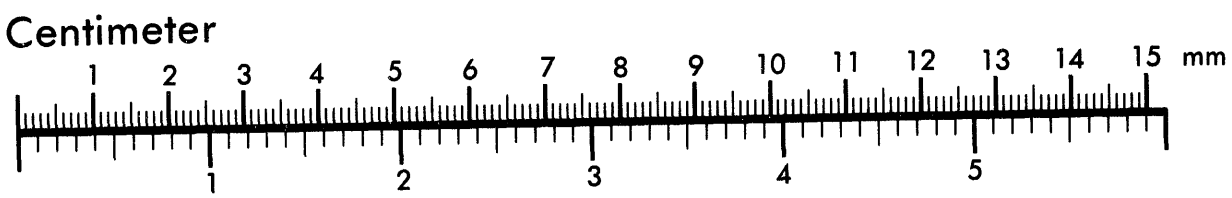

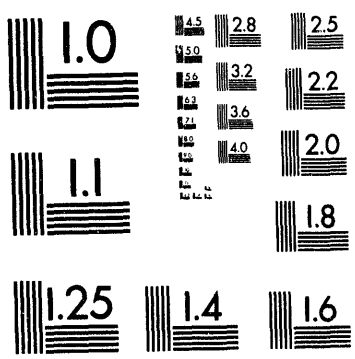

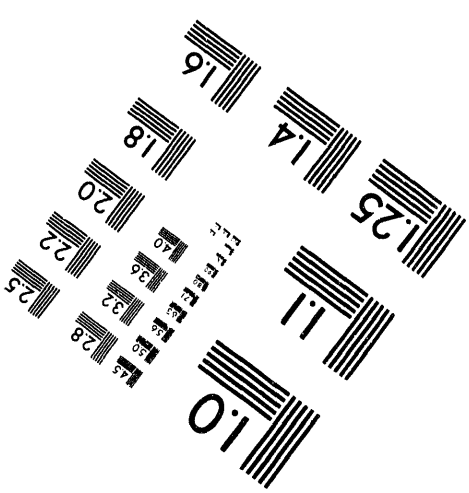

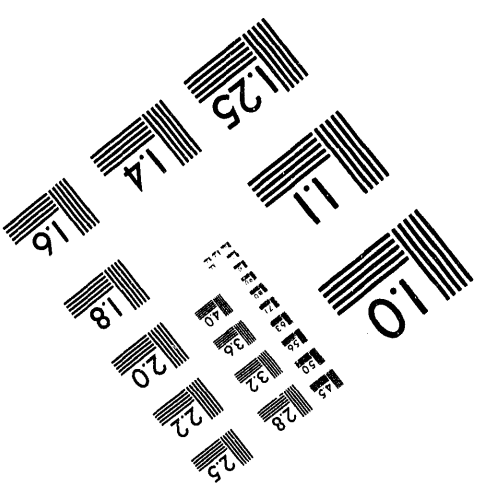

1 of 1

SIGNATURE OF THE CuO_2 PLANE RELATED BANDS IN $YBa_2Cu_3O_{6.9}$ AS SEEN BY ANGLE-RESOLVED PHOTOEMISSION*

M. Lindroos[1], A. Bansil[1], K. Gofron[2,3], J. C. Campuzano[2,3], H. Ding[2,3], R. Liu[2,4], and B. W. Veal[2]

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Signature of the CuO_2 plane related bands in $YBa_2Cu_3O_{6.9}$ as seen by Angle-resolved photoemission

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ABSTRACT

We present first-principles computations together with corresponding angle-resolved photoemission measurements in order to delineate the shape and polarization dependence of the spectral feature associated with the CuO_2 plane-related bands from the (001) surface of $YBa_2Cu_3O_{6.9}$. Theoretical predictions are found to be in remarkable agreement with the observed character of the spectral feature between 0 and 0.3 eV binding energy (for $k_{//}$ values along the Γ-S line), and indicate that the local-density-approximation based wave-functions implicit in our theory provide a reasonable description of the CuO_2 plane band states near the Fermi energy. Our computations also show that of the six possible surafce terminations, the ARPES spectra from Y123(001) surface are reasonably described by the BaO/CuO_2 ideal surface termination, i.e. by assuming a BaO layer followed by a CuO_2 plane layer below.

PACS Numbers: 71.10.+x, 71.25.-s, 74.70.Vy, 79.60.-i

An issue of contention since the discovery of the high-T_c superconductors has been whether or not electron-electron correlations invalidate the conventional local-density-approximation (LDA) based band theory framework for describing the electronic structure of these novel materials. The angle-resolved-photoemission (ARPES), positron-annihilation-angular-correlation and dHvA experiments have established that the archetypal compound $YBa_2Cu_3O_{6.9}$ possesses Fermi surfaces in essential accord with the LDA predictions. The existence of Fermi surfaces however does not imply the validity of the LDA Fermi-liquid picture, and it is important therefore to search for more discriminating tests of the theory [1-3].

With this motivation, we consider direct comparisons between the measured ARPES spectral intensities and the corresponding first-principles band theory predictions as a means of testing the underlying wavefunctions. We focus in particular on the bands associated with the CuO_2 planes which are widely believed to play a central role in the occurrence of high superconducting transition temperatures. Several authors have associated spectral features near the Fermi energy in the ARPES spectra from the $YBa_2Cu_3O_{6.9}$ (001)-surface with CuO_2 planes [4-8]. Here we specifically discuss how the intensity of this feature changes as the direction of polarization of the incident radiation is varied for a fixed value of the electron momentum parallel to the surface ($k_{//}$). The agreement between theory and experiment with regard to this characteristic signature of the CuO_2 planes gives confidence in the interpretation of the ARPES spectra and in the reasonableness of the conventional model implicit in the calculations.

On the theoretical side, we have generalized the one-step photoemission approach [9-10] in order to treat systems with arbitrary number of atoms in the unit cell. All existing work had been limited to a maximum of two atoms per layer unit cell [11], whereas the $YBa_2Cu_3O_{6.9}$ (001) surface requires at least *three* basis atoms, and a larger basis set for other low index faces. We emphasize that in the present one-step formulation the

photoemission process is treated as a single quantum mechanical event, and artificial distinctions between the processes of excitation, transport, and transmission of the electron through the surface barrier invoked in the earlier *ad hoc* three step type models are removed [12]. As is evident already from the experience on simpler materials, quantitative predictions of the ARPES intensities are not possible within the three-step formulation, and the use of the one-step approach which properly accounts for multiple scattering effects on the final as well as initial electron states is essential. Our new photoemission codes would also permit a first-principles treatment of ARPES spectra from complex materials more generally.

An overview of our theoretical methodology is as follows. The intensity of photoemitted electrons of a given energy E and emission direction $\mathbf{k}$ for incident radiation of frequency ω can be written in the one-step formalism as [10]

$$I = -\frac{1}{\pi}\mathrm{Im}\left\langle \mathbf{k}_{//}\left| G_2^+ \Delta G_1^+ \Delta^\dagger G_2^- \right| \mathbf{k}_{//}\right\rangle \qquad (1)$$

where G_2 and G_1 are the one-electron Green's functions at the final state energy ($E+\hbar\omega$) and the initial state energy E respectively; the superscripts +(-) on the Green's functions indicate forward (backward) propagation. Δ is the photon field operator. Practical photoemission intensity computations assume a semi-infinite solid in which atoms are represented by non-overlapping muffin-tin potentials, and the vacuum is separated from the bulk by a step V_{inner}, the 'inner potential'. The analysis of form (1) proceeds most naturally via the use of multiple-scattering theory and low-energy-electron-diffraction techniques. The key quantities are the scattering matrices associated with a single layer; we have generalized the original equations of Pendry [10,13] to the case of a general complex crystal. Note that since Y123 contains buckled layers, the layer scattering matrices no longer possess mirror symmetry. The layer scattering matrices permit the

evaluation of the wavefields in terms of which the integrations of Eq. (1) can be carried out to yield ARPES intensities.

Concerning computational details, we have used the structural data of Beno *et al.* [14]. Our muffin-tin potentials for various sites are based on the use of semi-relativistic self-consistent KKR methodology [15], and yield bulk band structure and Fermi surfaces of $YBa_2Cu_3O_7$ in reasonable accord with the well-known results, relatively small differences between various band structures notwithstanding. Following common practice, the self-energy corrections to the potential were incorporated via a semi-empirical step potential at the surface, i.e. $V_{inner} = V_R + iV_I$. V_R was taken to be 10.4 eV, estimated as the sum of the Fermi energy and the spectrometer work function. V_I was taken to be 2 eV for final states (electrons); for initial states (holes) an energy dependent value varying between 0.1 eV at the Fermi energy to about 1.0 eV at 3 eV binding energy was used. The present values of V_I and V_R are representative of measurements, but in any event, the results of this article are quite insensitive to the choices of these parameters, the computed spectral peaks of course being broader with increasing V_I.

The experiments were carried out at the Aladdin synchrotron, with a NIM monochromator giving a total energy resolution of 30 meV and an angular resolution of $\pm 1^\circ$. The photon beam was approximately 92% linearly polarized in the horizontal plane at 21.2 eV. The measurements involved twinned $YBa_2Cu_3O_{6.9}$ single crystals [16] of typical dimensions $1 \times 1 \times 0.1 mm^3$, and exhibited a sharp superconducting transition at 92K with a transition width of less than 2K as determined by a SQUID magnetometer. The samples were carefully oriented by Laue diffraction and cleaved *in situ* in a vacuum of 6×10^{-11} Torr at 12K. The orientation was confirmed by the observed symmetry of sharp photoemission features around high symmetry points (X, Y, and S) in the Brillouin zone (BZ).

Our purpose, as noted, is to investigate how the intensity of the ARPES spectral peak associated with the CuO_2 planes changes when the polarization vector of the incident light is rotated in the crystal a-b plane [17]. Fig. 1 shows two sets of spectra, both obtained from the same specimen when the light is incident at 45° to the surface normal, and in a plane containing the normal and a Γ–S line in the BZ. In Fig. 1(a), the detector also lies in the plane of incidence and different values of $k_{//}$ along Γ–S are measured by changing the polar angle of the detector. In Fig. 1(b), the orientation of the detector is in a plane perpendicular to the plane of incidence, so that k-states along another Γ-S line *perpendicular* (but equivalent) to the one in Fig. 1(a) are scanned. It is straightforward to show that for a general orthorhombic lattice, the spectra of Fig. 1(b) will be identical to the case where instead of the detector, the incident light beam is rotated by about 90°. In short then, the electric field vector of the incident light, in addition to a component along the crystal z-axis, possesses a component ***along*** the Γ-S direction in Fig. 1(a), but *perpendicular* to Γ–S in Fig. 1(b). We also obtained a third set of spectra using a different specimen which was mounted such that the incident beam is aligned 45° to the Γ-S line. Taken together, we thus have three sets of spectra with polarization, parallel, perpendicular, and at 45° to the Γ-S direction.

A number of other measurements we have carried out using a range of polar angles show that the spectral feature associated with the CuO_2 plane bands is insensitive to A_z, the component of the light vector potential perpendicular to the surface. Significantly, this experimental observation is in accord with our computations, which indicate that the CuO_2 plane bands are not excited by A_z. For this reason, we have mostly ignored A_z in our discussion, as for example is implicit in the directions of polarization vectors given in Fig. 1.

We are concerned with the feature lying between 0 and 0.3 eV binding energies in Fig. 1(b), which has been widely interpreted as the signature of two CuO_2 plane bands

moving across the Fermi energy [4-7,18]. Fig. 2(a) illustrates the polarization dependence of this feature in detail with the help of the 8° curves (thick lines) of Figs. 1(a) and 1(b). Fig. 2(b), which gives the corresponding computed spectra, shows that the shape and polarization dependence of the spectral feature associated with the CuO_2 plane bands is remarkably similar to the measurements [19]. The results of Fig. 2 are typical in that the calculated and measured spectra at nearby $k_{//}$ values display a similar behavior; the intensity of the CuO_2 plane bands is small for A // Γ-S and large for A $\perp\Gamma$-S.

Fig. 3 makes a quantitative comparison between the computed and measured polarization dependencies, and the agreement is excellent. For this purpose, great care was taken in obtaining experimental intensities. The measurements have been repeated on different samples, and at different times, and results very similar to those of Fig. 3 have been obtained. The agreement between theory and experiment seen in Fig. 3 is highly robust to variations such as small changes in the value of $k_{//}$, and whether or not some reasonable background (several different types were tried) is subtracted from the spectra in making such a comparison [20].

This study gives insight into the important question of surface termination in Y123. Ba-termination is suggested by the fact that Ba-core level shifts have been reported in Y123 [21]; this result however does not rule out the presence of other atoms on the surface, and does not determine which of the two Ba-terminations is prevalent. The real surface may of course be an admixture of various ideal terminations. Although we carried out computations for six possible ideal terminations admitted by the Y123 structure, all theoretical results in this article refer to the BaO/CuO_2 termination, i.e. a BaO layer followed by the CuO_2 plane layer. The reason is that we find that only the BaO/CuO_2 surface yields theoretical spectra which possess a shape similar to the measurements over the larger binding energy range of about 2 eV. As the insets in Fig. 2 show, both theory and experiment display the CuO_2 plane peaks near E_F followed by a much larger peak

around 1 eV. The differences in the absolute positions of the peaks seen in the insets are common in first-principles comparisons of this sort even in simpler materials, and may reflect effects of electron-electron correlations missing from the present LDA-based band theory framework, and also of possible deviations of real surface from an ideal one assumed here [22]. We emphasize however that the computed azimuthal dependence of the CuO_2 plane band peak was found to be essentially independent of the surface termination in all cases where plane band peaks could be identified, and thus the theoretical signature of the CuO_2 planes in Fig. 3 constitutes a rather discriminating test of the band theory predictions.

One may be tempted to conjecture that the agreement of Fig. 3 merely reflects the symmetry properties of the lattice and thus does not test the character of the underlying LDA band theory based wavefunctions. In this connection, we have repeated the calculations for other bands in Y123 (e.g. the Cu-O chain bands which give the electron ridge Fermi surface and the S-centered pillbox; none of these bands have however so far been identified in ARPES spectra, some hints notwithstanding) and found that the associated azimuthal intensity plots like those of Fig. 3 possess many different shapes, and even for the same band, this signature can vary between different terminations. For these reasons the presently observed agreement is not a simple consequence of the symmetry of the wave functions forced by that of the crystal lattice [23].

In summary, we have shown that the detailed shape and polarization dependence of the spectral feature associated with CuO_2 plane bands, as obtained from the LDA band theory framework, is in remarkable accord with the ARPES measurements. This result constitutes a discriminating test of the underlying band theory based wavefunctions implicit in the computations. We also find that the ARPES spectra from the Y123 (001) surface are reasonably described by the BaO/CuO_2 ideal surface termination. ARPES experiments on Y123 films with different terminations should be most worthwhile.

We thank Roy Benedek for important conversations. This work was supported by the DOE under contract W-31-109-ENG-38, including a subcontract to Northeastern University, NSF grant DMR8914120, a travel grant under the US-Finland program of the NSF, the Academy of Finland, and benefited from the allocation of supercomputer time at NERSC, and the San Diego Supercomputer Center, National Science Foundation Science and Technology Center for Superconductivity under Contract #DMR-8809854(RL).

Figure Captions

Fig. 1: ARPES spectra from a twinned $YBa_2Cu_3O_{6.9}$ single crystal for polarization (a) parallel and (b) perpendicular to the Γ-S direction. The insets show the Fermi surface of Y123 projected on the Γ-X-S-Y plane [24]. The solid dots in the insets give the $\mathbf{k}_{//}$ values for various spectra (the polar angle of the detector is indicated next to each spectrum). The double arrows denote the polarization direction of incident light. The thick curves for polar angle of 8° are used in Fig. 2(a).

Fig. 2: Typical experimental and theoretical ARPES spectra for $\mathbf{A} // \Gamma$-S and $\mathbf{A} \perp \Gamma$-S in the vicinity of the Fermi energy displaying the polarization dependence of the CuO_2 plane band feature. The experimental data in Fig. 2(a) give the 8° spectrum of Fig. 1. The insets show the shapes of the spectra over a larger binding energy range for $\mathbf{A} // \Gamma$-S (thin lines) as well as $\mathbf{A} \perp \Gamma$-S (thick lines).

Fig. 3: The computed intensity of the CuO_2 plane band feature as a function of the azimuthal angle of polarization of the incident light (solid curve) for a fixed value of $\mathbf{k}_{//}$ (along the Γ-S direction). The experimental results are given by filled circles on which the direction of the polarization vector is shown by double arrows. The normalization between theory and experiment was determined by setting the peak height in Fig. 2(a) for $\mathbf{A} \perp \Gamma$-S to equal that of the corresponding theoretical peak in Fig. 2(b).

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1. There is extensive literature dealing with the issues mentioned in this paragraph. Refs. 2 and 3 are recent examples with further citations.

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16. One might think that it would be preferable to use *untwinned* crystals. However, straightforward symmetry arguments show that insofar as emission along the Γ-S direction in Y123 is concerned, the effects of polarization can be studied via twinned specimens.

17. The simplest approach obviously is to use normally incident linearly polarized light and rotate either the plane of polarization or the sample and the detector synchronously. Such an approach however is not possible with our experimental setup because the synchrotron light is horizontally polarized and our cooling coils allow only limited movement.

18. Theoretically, the spectra, when followed as a function of $k_{//}$ show two peaks crossing the Fermi energy corresponding to the two CuO_2 plane bands. In Fig. 2(b), one of these plane band peaks has moved above the Fermi energy.

19. A weak feature is seen around 0.4 eV binding energy in the theoretical spectra of Fig. 2(b). This may correspond to the feature which seems to be present in the measurements around 0.8 eV in Fig. 1(b).

20. The theoretical results of Fig. 3 neglect A_z We have however carried out a number of calculations in which the effects of A_z are included, and find that the presence of A_z generally yields somewhat less symmetric curves than those of Fig. 3.

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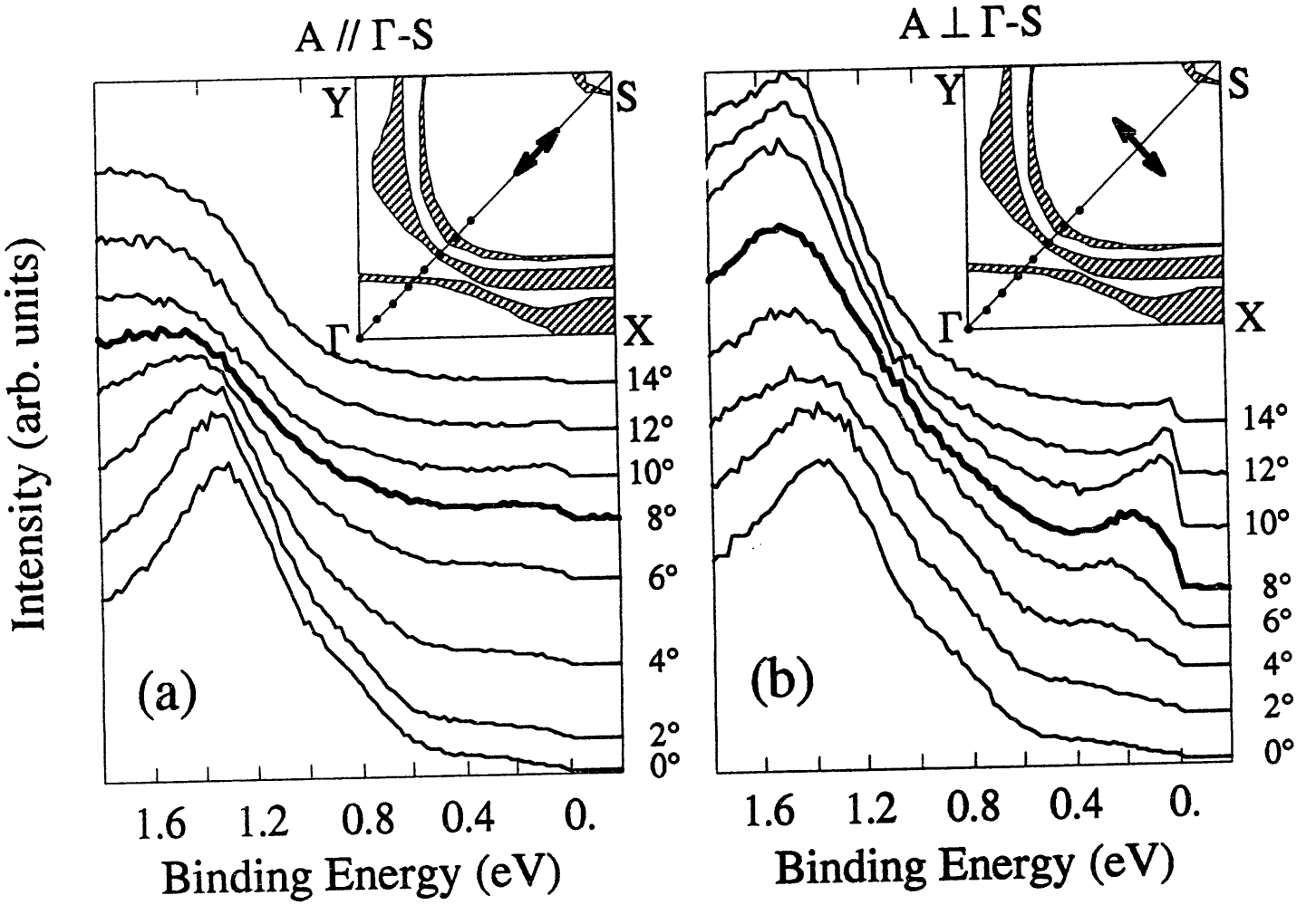
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A ⊥ Γ-S
Y
S
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12°
10°
8°
6°
4°
2°
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(a)
(b)
Intensity (arb. units)
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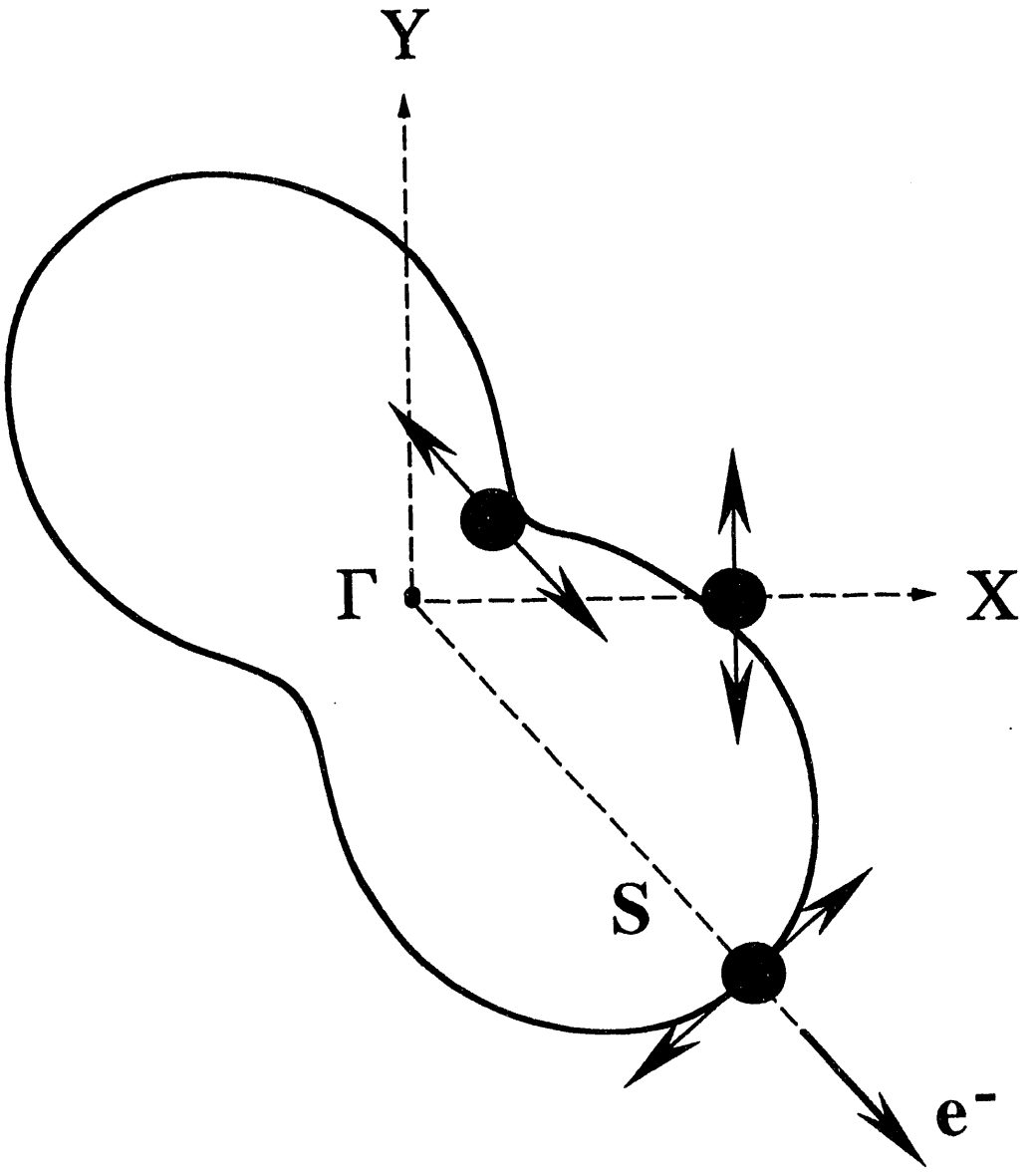
1.2
0.8
0.4
0.
Binding Energy (eV)


Y
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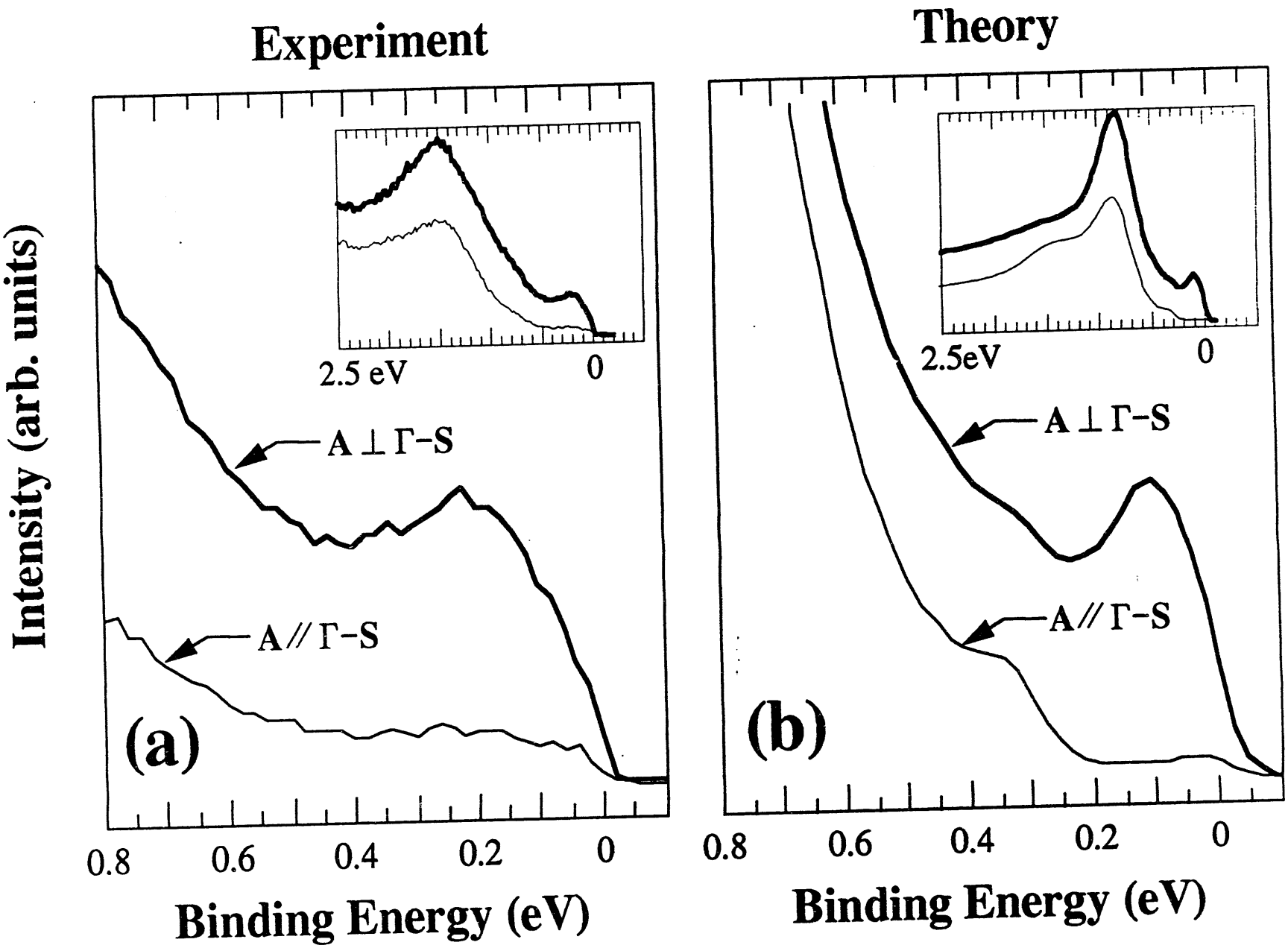
Experiment
Theory
Intensity (arb. units)
2.5 eV
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2.5eV
0
A ⊥ Γ-S
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(a)
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