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May 23, 1996

Dr. Deborah Van Vechten
ONR, Code 312
Arlington, VA 22217

Dear Dr. Van Vechten:

Enclosed is the yearly report for Contract # N00014-95-1-0760 entitled "High Resolution Photoemission Studies of Interfaces in High-Tc Superconductors". We are sending copies of this report to the following people:

Contract Officer (Van Vechten)	3 copy
Admin. Grants Officer (Linden Clausen)	1 copy
Director Naval Research Laboratory	1 copy
✓Defense Technical Information Center	2 copies
Office of Naval Research	1 copy

Sincerely,

Zhi-xun Shen

Zhi-xun Shen

cc: Sponsored Projects Office
C.M.R. (Susan Stout)

Note: C.M.R. is now handling this contract for us. The phone no. for Susan Stout is: 415-723-0197.

DEPARTMENT OF THE NAVY
OFFICE OF NAVAL RESEARCH
SEATTLE REGIONAL OFFICE
1107 NE 45TH STREET, SUITE 350
SEATTLE WA 98105-4631

IN REPLY REFER TO:

4330
ONR 247
11 Jul 97

From: Director, Office of Naval Research, Seattle Regional Office, 1107 NE 45th St., Suite 350, Seattle, WA 98105

To: Defense Technical Center, Attn: P. Mawby, 8725 John J. Kingman Rd., Suite 0944, Ft. Belvoir, VA 22060-6218

Subj: RETURNED GRANTEE/CONTRACTOR TECHNICAL REPORTS

1. This confirms our conversations of 27 Feb 97 and 11 Jul 97. Enclosed are a number of technical reports which were returned to our agency for lack of clear distribution availability statement. This confirms that all reports are unclassified and are "APPROVED FOR PUBLIC RELEASE" with no restrictions.

2. Please contact me if you require additional information. My e-mail is *silverr@onr.navy.mil* and my phone is (206) 625-3196.

ROBERT J. SILVERMAN

Yearly Report

High Resolution Photoemission Studies of Interfaces in High-Tc Superconductors

N00014-95-0760

Department of the Navy

3-1-95 to 2-28-98

P.I.: Prof. Z.X.Shen
Stanford University
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Stanford, CA 94305-4045

Angle-resolved photoemission studies of high-temperature superconductor interfaces and surfaces

Z.-X. Shen, Stanford University

Our research has involved using angle-resolved photoemission spectroscopy (ARPES) as a nano-scale probe of the electronic structure of surfaces and interfaces of high-temperature superconductors. Photoemission has provided unique and valuable information because of its surface sensitivity, excellent energy resolution, and ability to detect core-level chemical shifts. The information has strong implications for a fundamental understanding of the electronic structure of the cuprates as well as the construction of practical devices such as Josephson junctions. We will focus on: (1) description of custom-designed thin film samples of high temperature superconductors (HTSC) and the development of methods to study them with ARPES, (2) electronic structure measurements using ARPES, including the measurement of energy gaps, (3) the implications for characteristics of devices using HTSC, and (4) proximity effect searches.

Our thin film samples have come from a collaboration with a group at Varian Associates (J. N. Eckstein and I. Bosovic). The high quality thin films of BiSrCaCuO (BSCCO), e.g. $Bi_2Sr_2Ca_{1-x}Dy_xCu_2O_{8+\delta}$ (Dy-Bi2212), are grown by atomic layer-by-layer molecular beam epitaxy (ALL-MBE). The growth method allows very precise control of layer sequences and doping. Novel structures such as Bi-2278 have been produced. The doping of holes in the CuO_2 planes of BSCCO is controlled by both the dysprosium and the oxygen content, both of which can be varied over a large range. We have developed the top-post method of cleaving the films in ultra-high vacuum to expose fresh surfaces, and it is now reliable enough to be routine. The surfaces of cleaved films are extremely flat, and this helps in getting very good angular resolution and consequently good k-space resolution in ARPES. We have succeeded in measuring aspects of the electronic structure in these films including the shape of the Fermi surface and anisotropic superconducting state gaps.

The measurement of superconducting energy gaps with ARPES has proven to be very informative. We have recently studied the gap in Dy-doped Bi2212 films as a function of temperature, doping and angle. In addition to the anisotropic gap in the superconducting state previously seen in optimally-doped BSCCO single crystals, we have found that the underdoped samples (those with doping less than that required for highest T_c) show a gap in the *normal* state. The normal state gap is very similar in its magnitude and strong angular dependence to the superconducting state gap, implying a common underlying pairing mechanism. The data are consistent with a $d_{x^2-y^2}$ gap both above and below T_c as can be seen in Fig. 1. The gap (at fixed temperature) is plotted against $0.5|\cos k_x a - \cos k_y a|$ to compare with the d-wave prediction which is a straight line on this plot. The flattening near the origin may be accounted for with impurity scattering, the so-called "dirty d-wave" scenario. Another surprising observation is the failure of the gap to fall proportionally to T_c as the sample is underdoped, as would be expected from the familiar BCS mean-field theory. In fact, the gap is observed to go up slightly as T_c drops (Fig. 2 inset). For comparison, the d-wave BCS prediction is plotted as a dashed line, and it shows the opposite trend from the data. For comparison to phase diagrams, Fig. 2 shows the superconducting state gap Δ_{sc} vs. hole concentration δ. Once again, the conventional expectation (dashed line) is violated. These two observations (normal state gap and non-mean-field gap vs. T_c dependence) taken together have strong implications for superconductivity in cuprates. In particular, they imply that the gap has a different energy scale than kT_c. A consistent picture is the following: d-wave pairing of electrons begins at a temperature proportional to the gap, but phase fluctuations in the order parameter severely depress

T_c in underdoped and possibly optimally doped samples. This understanding may lead to new ways to search for and design HTSC. A possibility is to grow multilayer samples with different functional groups.

There are several implications of this work for device applications. One reason is that surfaces and interfaces of HTSC have a tendency to lose oxygen, making them underdoped. Thus the electronic structure of underdoped BSCCO is directly relevant. An example comes from the thin film multilayer structures from the Varian group. They construct tunnel junctions consisting of, for example, Bi2212 / 0278[Dy] / Bi2212 using the same MBE growth method. The center block consists of a stack of eight CuO2 layers separated by Ca, with Dy substituting for Ca in the middle. The Dy produces an insulating tunnel barrier by depleting holes. In addition to observing Josephson currents with a high I_cR_n product of 10 mV, the Varian group also sees features in the I-V curves at higher energies, around 50 mV. The energy scale for this effect is quite similar to the energy scale of the normal state gap we have seen with photoemission. It is natural to relate the pseudo-gap behavior in the tunnel junctions to the existence of severely underdoped CuO_2 layers near the Dy-doped layers. Photoemission is thus able to give detailed information about electronic structure relevant to constructing useful devices. In general, photoemission can be used as a diagnostic to identify underdoped cuprates from the characteristic broad lineshape near momentum (π,0).

Other work (still underway) using ARPES is the direct characterization of the Bi2278 thin films already mentioned. It appears that there is some k_z dispersion in the photoemission data which, if confirmed, would imply coherent charge transport along the *c*-axis and allow a deeper understanding of devices (such as Josephson junctions) that involve current flow perpendicular to the planes.

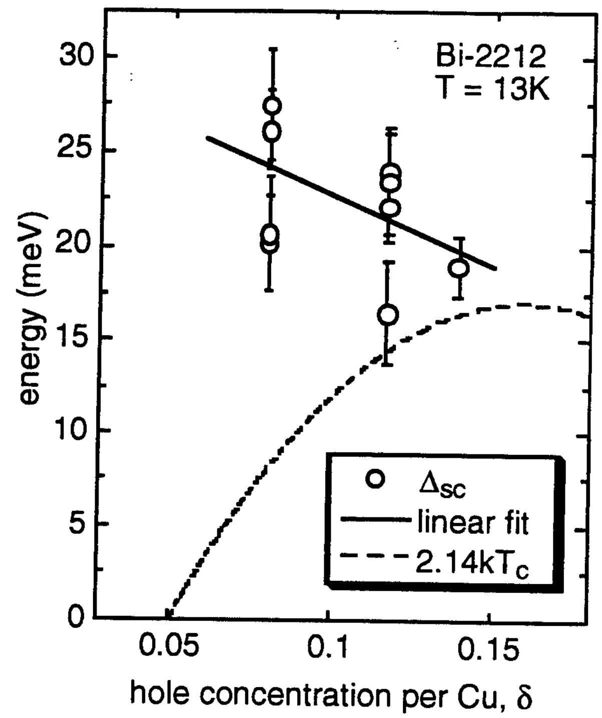
Finally, we have searched for the proximity effect, or the leaking of Cooper pairs from a superconductor into a neighboring metal in close electrical contact. The proximity effect is important in SNS junctions and also in preparing passivated surfaces of a HTSC that are still superconducting. Our ongoing work has so far involved deposition of Au on top of a freshly cleaved BSCCO surface. We then look for a shift in the leading edge of energy distribution curves of the Au layer that would be indicative of a (possibly anisotropic) gap induced by proximity effect coupling to the underlying BSCCO superconductor. This experiment requires excellent energy resolution to succeed.

Fig. 3 shows photoemission data obtained from a BSCCO samples covered with two to three atomic layers of Au (5-7 Å) from an evaporator after cleaving in ultra-high vacuum (10^{-11} Torr scale). The *k*-space point is (π,0), the region of maximum gap for pure BSCCO. The position of the leading edge has been obtained by fitting to a Fermi function. The result is that the gap, if present, is smaller than the error bars of our measurement. The only significant difference in the spectra is the sharpening of the edge, as expected from a reduction in temperature. The positions of the leading edges at 10 K and 100 K are at binding energies of 4.7 ± 0.7 meV and 3.5 ± 0.8 meV, respectively. This places a stringent limit on the magnitude of the superconducting gap in Au of 2 to 3 meV, using the criterion of the leading edge position.

This value is surprising since the proximity effect of Au with a conventional superconductor can extend many hundreds of Angstroms. Either there is an intrinsic limitation on the proximity effect with high T_c superconductors (possibly related to very short *c*-axis coherence lengths or pairing symmetry), or the interface is not sufficiently clean. The second possibility is unlikely, however, since our group has shown previously that junctions of BSCCO and Au prepared in ultra-high vacuum at low temperatures are extremely clean and abrupt. For the present, the proximity effect from HTSC with conventional metals appears surprisingly weak.

Angle-Resolved Photoemission Study of High-T_c Surfaces and Interfaces

Z.-X. Shen, Stanford University



Technology Issues:

- Applications include Josephson junctions, SQUIDS, microwave filters
- Surface passivation methods
- Effect of doping levels on device performance

Objectives:

- To understand the change in superconducting and normal state electronic structure with doping
- To develop methods of characterizing surfaces of superconducting thin films
- To study interfaces layer by layer with angle-resolved photoemission
- To understand the fundamental mechanism of superconductivity in cuprates

Approach:

- Study MBE-grown BSCCO thin films using high energy-resolution angle resolved photoemission spectroscopy
- Prepare fresh film surfaces in UHV, characterize with ARPES, XPS, and LEED
- Look for changes from underdoping in films with Dy^{3+} substituting for Ca^{2+}

Accomplishments:

- Developed cleaving procedure for preparing thin film surfaces of near atomic-level perfection
- Developed a means of characterizing the doping level from ARPES lineshape near $k_{||} = (\pi,0)$
- Doping study of Dy-Bi2212 supports idea of "pre-formed pairs" of electrons, suggests phase fluctuations are limiting T_c
- Preliminary study of 8-plane Bi2278 seems to show k_z dependence

Impact:

- Collaboration with Varian to characterize their MBE BSCCO films used in Josephson junctions

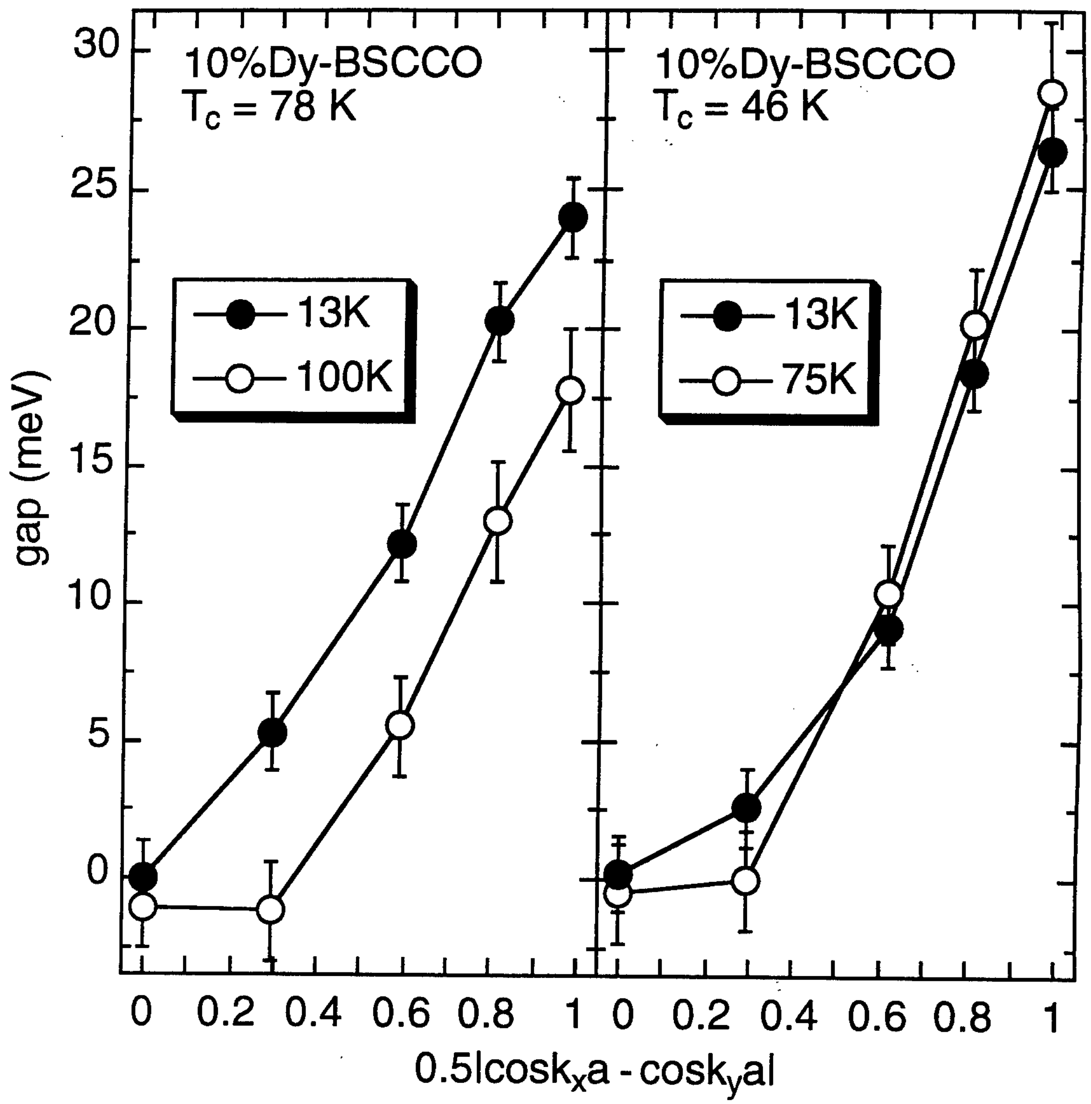
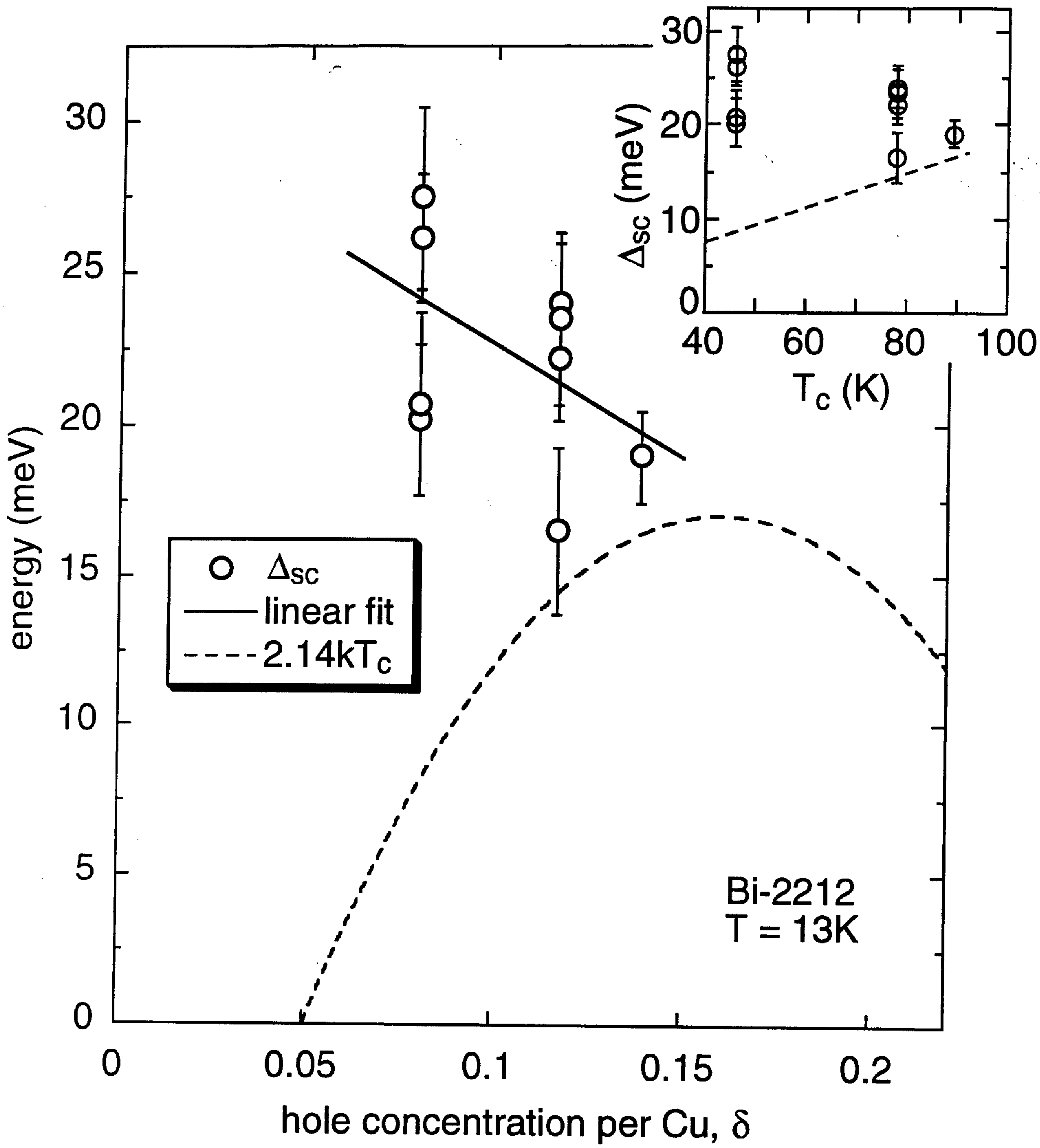

10%Dy-BSCCO
T_c = 78 K
10%Dy-BSCCO
T_c = 46 K
13K
100K
13K
75K
gap (meV)
0 5 10 15 20 25 30
0 0.2 0.4 0.6 0.8 1
0.5|cosk_xa - cosk_ya|

Figure 1



30
25
20
15
10
5
0
energy (meV)
0
0.05
0.1
0.15
0.2
hole concentration per Cu, δ
Δsc
linear fit
2.14kTc
Bi-2212
T = 13K
Δsc (meV)
Tc (K)
40
60
80
100

Figure 2

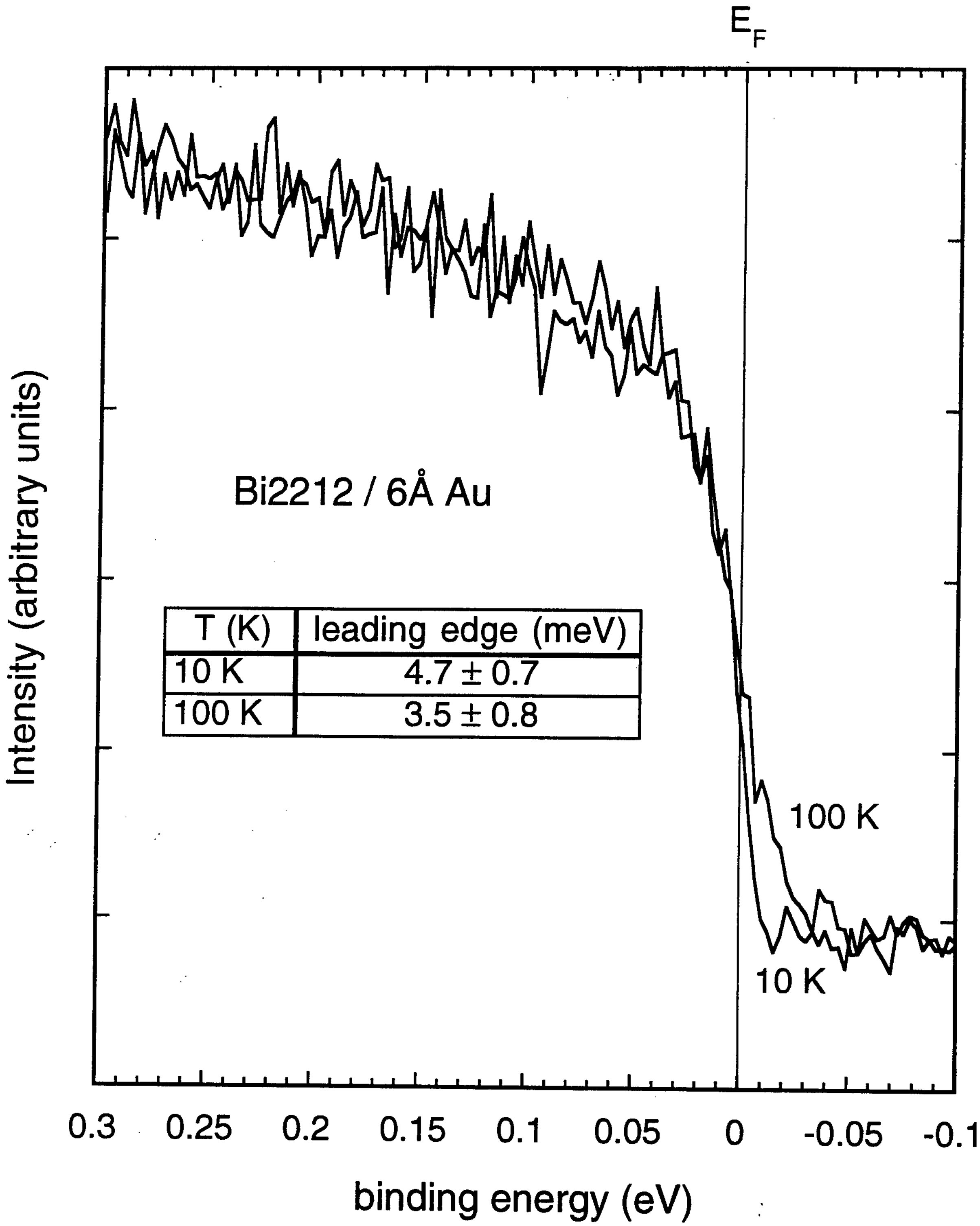

E F
Bi2212 / 6Å Au
T (K) | leading edge (meV)
10 K | 4.7 ± 0.7
100 K | 3.5 ± 0.8
100 K
10 K
Intensity (arbitrary units)
0.3
0.25
0.2
0.15
0.1
0.05
0
-0.05
-0.1
binding energy (eV)

Figure 3