

Lawrence Berkeley National Laboratory

Recent Work

Title

HIGH-RESOLUTION X-RAY PHOTOEMISSION SPECTRUM OF THE VALENCE BANDS OF GOLD

Permalink

<https://escholarship.org/uc/item/8rx4x7ns>

Author

Shirley, D.A.

Publication Date

1971-11-01

Submitted to Physical Review
RECEIVED
LAWRENCE
BERKELEY LABORATORY

LBL-277
Preprint

C.2

LIBRARY AND
DOCUMENTS SECTION

HIGH-RESOLUTION X-RAY PHOTOEMISSION
SPECTRUM OF THE VALENCE BANDS OF GOLD

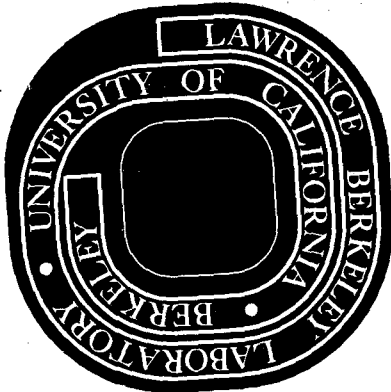
D. A. Shirley

November 1971

AEC Contract No. W-7405-eng-48

TWO-WEEK LOAN COPY

*This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 5545.*



LBL-277

C.2

H

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

HIGH-RESOLUTION X-RAY PHOTOEMISSION SPECTRUM OF THE VALENCE BANDS OF GOLD*

D. A. Shirley

Department of Chemistry and
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

November 1971

ABSTRACT

High-resolution gold valence-band photoemission spectra of gold were obtained by the use of monochromatized Al K α radiation and a single-crystal specimen. After background and scattering correction were made, the results were compared directly with broadened theoretical density-of-states functions. The following conclusions were drawn: (i) Relativistic band structure calculations are required to fit the spectrum. (ii) Both the KKR calculation of Connolly and Johnson and the RAPW calculation by Christensen and Seraphin give density of states results that (after broadening) follow the experimental curve closely. (iii) Full Slater exchange is required: fractional (2/3 or 5/6) exchange gives d band densities of states that are far too wide. (iv) Eastman's 40.8 eV ultraviolet photoemission spectrum is similar to the x-ray spectrum, suggesting little dependence on photon energy above 40 eV. (v) Both (ii) and (iv) imply an absence of strong matrix-element modulation in the photoemission spectrum.

I. INTRODUCTION

Electronic band structures are of fundamental importance in understanding properties of metals. A knowledge of the valence-band density of states of a metal can in principle yield considerable information about that metal's band structure. X-ray photoemission experiments, in which valence electrons are ejected from the specimen by photons from a monochromatic source and energy-analyzed in an electron spectrometer, yield spectra that are closely related to the valence-band density of states. The extent to which these photoemission spectra and the density of states can be directly compared is still somewhat uncertain, however.

In this paper the high-resolution x-ray photoemission spectrum of the valence band in a gold single crystal is reported. The spectrum is compared with lower-energy photoemission spectra and with band-structure results. The following questions are at least partially answered: (1) Do ultraviolet photoelectron spectroscopy (UPS) results approach x-ray photoelectron spectroscopy (XPS) data as the UV photon energy increases toward the upper end of the readily available energy range (~ 40 eV)? (2) Is it meaningful to compare XPS spectra directly with valence-band densities of states, or are matrix-element modulation effects so large as to obviate such comparisons? (3) Can XPS spectra establish the necessity for relativistic band structure calculations in heavy elements? (4) Are XPS spectra sensitive enough to distinguish critically among different theoretical band-structure calculations?

Experimental procedures are described, and results are presented, in Sec. II. In Sec. III these results are compared with theory and addressed to the above questions.

II. EXPERIMENTAL

A gold single crystal of 99.9% purity was cut to provide samples with (100), (110), and (111) faces. These were polished, etched, and annealed. Spectra were taken, at room temperature and in a sample chamber pumped to about 10^{-7} Torr, on a Hewlett-Packard ESCA spectrometer. This spectrometer employs monochromatized aluminum $K\alpha_{1,2}$ (1486 eV) radiation: it should in principle be possible to reduce the previously obtainable instrumental resolution^{1,2} of 1.0 eV by a factor of two or more. The spectrum given below shows a definite improvement over earlier spectra.

Under the above experimental conditions, which would be inadequate for most metals, gold is expected to retain a surface that is relatively free of absorbed gases. That the active sample³ was in fact predominantly gold metal was demonstrated by monitoring the Au $N_{VI,VII}$ doublet, which was very clean. In addition the oxygen 1s line and carbon 1s line were barely detectable, whereas both are large in a sample which has a layer of oxide. More detailed surface studies under carefully controlled conditions are planned. Meanwhile, the rather conservative conclusions given below are believed to be justified in light of the sample conditions described above.

Spectra from specimens in the three crystal orientations were very similar. A (110) spectrum, which had the best statistical accuracy, was analyzed for comparison with theory. The data reduction procedure consisted of three steps. First, the raw data were smoothed several times by the use of the relation

$$I_S(N) = [I(N-1) + 2I(N) + I(N+1)]/4 \quad (1)$$

Here $I(N)$ is the intensity in channel N after the smoothing operation. The main purpose of this step is the elimination of small systematic variations in

intensity, of instrumental origin. These data were smoothed six successive times; this had only a negligible effect on spectral resolution. A plot of the result is shown in Fig. 1.

The second data-reduction step was background subtraction. The position of the Fermi energy was easily identified in the raw spectrum by a step in the intensity (it was also established by the decelerating voltage of the electrostatic spectrometer). The spectral intensity was very constant above this energy. This intensity, I_B , was taken as background and was subtracted from the intensity throughout the valence-band energy range (i.e., for $-9.5 \text{ eV} \leq E - E_F \leq 1 \text{ eV}$). The intensity in channel N after this correction is denoted by $I'_S(N)$. Thus

$$I'_S(N) = I_S(N) - I_B \quad (2)$$

This correction is always necessary for x-ray photoemission spectra. The background in most spectrometers arises largely from photoelectrons that are ejected by high-energy bremsstrahlung and that undergo subsequent energy loss in the sample. This source of background is not present in the Hewlett-Packard spectrometer, because of monochromatization of the exciting radiation, but contributions from detector noise remain.

The final data-reduction step was a correction for inelastic scattering. In earlier work¹ this correction was made by the use of a response matrix. For the present data a simpler procedure was possible because there were no satellite x-ray peaks and a correction was necessary only for a constant inelastic tail.⁴ In making the correction it was observed that the spectrum returned to a constant level at kinetic energies below those of the valence bands. This level was somewhat higher than the baseline above the valence levels. The difference was

assumed to arise entirely from valence-band photoelectrons that were inelastically scattered before leaving the sample. This interpretation has been qualitatively well established by earlier work,¹ but it could be slightly wrong in detail. Even if it is, however, the corrected spectrum would be only slightly affected, and the interpretations given below would not be affected.

The inelastic-scattering correction was made by subtracting from $I'_S(N)$ a quantity proportional to the valence-band area at higher energies, to give $I''_S(N)$, under the condition $I''_S(0) = 0$. Here the double-prime notation denotes the intensity after correction for scattering, and channel 0 represents an energy just below the valence bands. Thus

$$I''_S(N) = I'_S(N) - I''_S(0) \left[\frac{\sum_{N' > N} I'_S(N')}{\sum_{N' > 0} I'_S(N')} \right] \quad (3)$$

This equation should in principle be iterated, but iteration was unnecessary for the gold spectrum because the correction was small. Figure 1 shows I'_S and I''_S together, to indicate the effect of data reduction on the spectrum.

III. COMPARISON WITH THEORY

The final corrected spectrum I_S'' should be closely related to the density-of-states function $\rho(E)$ that may be obtained, by sampling procedures, from band-structure calculations. An XPS spectrum is not expected to be affected significantly by the final-state density of states (as is the case in UPS) because at energies in the 1.5 keV range the density of states should be essentially featureless. There are other reasons that a direct comparison of I_S'' and $\rho(E)$ may not be valid. These were discussed in some detail earlier.¹ The conclusion was drawn that it would be difficult to estimate the extent to which I_S'' should resemble $\rho(E)$. The approach taken below is simply to plot the two together for comparison.

Non-relativistic band structure calculations give density-of-states histograms differing from I_S'' so much that there is no value in plotting them. Such a plot was made earlier for platinum.¹ The good agreement of the two-peak form of I_S'' with relativistic band-structure calculations appears on the other hand to establish immediately that relativistic effects must be considered in discussing the band structure of gold. This has been pointed out earlier by Smith⁵ and by Smith and Traum.⁶

Six theoretical results are available for the relativistic band structure of gold. Sommers and Amar⁷ used the Korringa-Kohn-Rostoker (KKR) approach. They did not give $\rho(E)$, so a direct comparison with I_S'' is not possible. It is clear, however, that their results give a valence band width considerably larger than the experimental width. This has been attributed by Christensen and Seraphin⁸ to the use of 2/3 Slater exchange by Sommers and Amar. Indeed, in another KKR calculation Connolly and Johnson⁹ used full Slater exchange and obtained a smaller valence band width that agrees well with experiment.

Three relativistic augmented-plane-wave (RAPW) calculations of the valence band structure of gold have been reported. Ramchandani^{10,11} used full (1), 5/6, and 2/3 Slater exchange, and concluded that full exchange was best. On comparison of his density-of-states histograms with I_S'' , it is obvious by inspection that his full-exchange results are in reasonable agreement with I_S'' , while the other two are not even remotely similar. Kupratakuln,¹² on the other hand, has done essentially the same calculation, also with full, 5/6, and 2/3 exchange, and has concluded that the best results are obtained with an exchange coefficient of 19/24. Detailed comparisons of the two sets of results shows that they are in serious conflict, with Kupratakuln's results showing extreme sensitivity to the exchange coefficient and his "19/24" band structure being in reasonably good agreement with Ramchandani's full exchange results. Christensen and Seraphin⁸ have also reported an RAPW calculation, with full Slater exchange. The energy bands in this case resemble Ramchandani's full exchange results and Kupratakuln's "19/24" exchange results much more closely than the 5/6 or 2/3 exchange results of the former or the full or 2/3 results of the latter. Apparently Kupratakuln has used a different Slater exchange coefficient scale factor than the authors of Refs. 7-11.

Smith and Traum⁶ have simulated a relativistic band structure by an interpolation scheme due to Hodges, Ehrenreich, and Lang¹³ and Ehrenreich and Hodges.¹⁴ This scheme inserts spin-orbit coupling into nonrelativistic band structure results.

Theoretical $\rho(E)$ functions are reported as histograms. As such they cannot be readily compared with experimental spectra, because the latter are broadened by instrumental resolution and relaxation effects.¹ For this reason

the theoretical histograms were broadened before the comparison was made. First, the histogram was converted into digital form by measuring the lengths of the bars in the published histograms. Next, broadening was done by a smoothing operation similar to that given in Eq. (1). The operation was repeated until the theoretical $\rho(E)$ was judged to resemble I_S'' most closely, for each case. Table I lists ΔE_p , the full width at half-maximum height, for the (optimized) broadening applied to each theoretical curve. Also listed are ΔE_d , the full width at half-maximum height of the d bands, and $E_F - E_d$, the energy difference between the Fermi energy and a point on the higher d-band peak that is half the peak height. The last two quantities were evaluated before and after broadening, to insure that the broadening process did not distort their values.

Finally, each broadened theoretical $\rho(E)$ curve was multiplied by a scale factor that made it about the same average height as I_S'' . Each $\rho(E)$ is plotted with I_S'' , separately, in Figs. 2-6.

IV. DISCUSSION

Cursory inspection of Table I and Figs. 2-6 shows that the overall agreement between theory and experiment is good. The quality of agreement varies sufficiently, however, to favor some of the theoretical curves over others, and to draw some useful conclusions.

Connolly and Johnson's results (Fig. 2) for $\rho(E)$ follow the experimental curve very closely. The d-band widths are in essentially perfect agreement. The position of Connolly and Johnson's d-bands is 0.1 to 0.2 eV closer to E_F than the experimental value. The spectral shapes are very close (perhaps surprisingly so), with the smaller low-energy peak showing slightly poorer agreement than the high energy peak. The more intense component of the low-energy peak lies at -5.7 eV (theoretical) vs -6.15 eV (experimental). Even if the d bands were lowered in energy to coincide overall better with experiment, the experimental intensity of the smaller component of the lower-energy peak would be much smaller than theoretical. This is presumably a consequence of its s-like character, which would imply a lower photoemission intensity than that of d electrons. The very good overall agreement in this case indicates that the relativistic KKR method can yield very good results for the gold d bands. Since full Slater exchange was used in the Connolly and Johnson calculation, giving correct d band widths, while the Sommers and Amar KKR calculation, with 2/3 Slater exchange, gave bands that were far too wide, full Slater exchange is clearly preferred for a relativistic KKR calculation.

Although the same principal features of the valence d bands are visible in Ramchandani's RAPW calculation (Fig. 3), detailed agreement is absent. Christensen and Seraphin have attributed the lack of agreement between Ramchandani's calculation and their own (both RAPW, with full exchange) to the use by Ramchandani of a matrix too small to achieve convergence.

Kupratakuln's RAPW results, with $19/24$ exchange, are fairly close to experiment (Fig. 4), but his d bands are too narrow. Because his exchange scale factor appears to differ from that of the other calculations, little more can be said about this result.

The full-exchange RAPW curve of Christensen and Seraphin (Fig. 5) follows the experimental spectrum about as well as did that of Connolly and Johnson. The former appears to reproduce the d band position slightly better, while the latter has a slight edge in regard to d band width. Both, however, show very good agreement with experiment. If the spectra can be made slightly sharper in the future, it may become feasible to make a detailed analysis of the components of each of the two main peaks in terms of individual energy bands.

The interpolated band-structure results of Smith and Traum (Fig. 6) give a good representation of the experimental spectrum at high energies, but their band width is about 0.4 eV large.

In an earlier paper¹ it was predicted that valence-band ultraviolet photoemission spectra, which vary strongly with energy, should approach XPS spectra as the photon energy is raised. This prediction is nicely confirmed for gold by comparing the spectra of Eastman and Cashion¹⁵ between 10.2 and 26.9 eV and the (low-resolution) 40.8 eV curve by Eastman¹⁶ with the present results. The good agreement between the 40.8 eV on 1483 eV spectra, together with their agreement with theoretical $\rho(E)$ curves, strongly suggest that "matrix-element modulation"¹⁷ of these spectra is a small effect. The reason for this is not well understood.

ACKNOWLEDGMENTS

Dr. A. Malera was most helpful in running many gold spectra on the Hewlett-Packard ESCA Spectrometer. Professor G. Somorjai generously provided a gold crystal and instructions on how to prepare it. Mrs. Winifred Heppler prepared the specimens and, together with Mrs. Penny Fink and Mr. James Davis, assisted in data reduction. The author also had helpful discussions and/or communication with Prof. Marvin Cohen, Dr. Dean Eastman, Dr. Neville Smith, and Prof. J. W. D. Connolly.

FOOTNOTES AND REFERENCES

- * Work performed under the auspices of the U. S. Atomic Energy Commission.
1. C. S. Fadley and D. A. Shirley, J. Res. Natl. Bur. Std. 74A, 543 (1970).
 2. Y. Baer, P. F. Hedén, J. Hedman, M. Klasson, C. Nordling, and K. Siegbahn, Physica Scripta 1, 55 (1970).
 3. The mean depth from which photoelectrons of this energy are ejected without loss from gold is about 20\AA .
 4. The existence of this tail has been established for a number of core-electron peaks.
 5. N. Smith, Bull. Am. Phys. Soc. Ser. II 16, 414 (1971). The importance of relativistic effects in gold was clearly established in this talk.
 6. N. V. Smith and M. U. Traum, "Spin Orbit Coupling Effects in the Ultraviolet and X-Ray Photoemission Spectra of Metallic Gold", to be published in "Electron Spectroscopy", ed. by D. A. Shirley (North-Holland, 1972).
 7. C. B. Sommers and H. Amar, Phys. Rev. 188, 1117 (1969).
 8. N. E. Christensen and B. O. Seraphin, Phys. Rev. B, to be published.
 9. J. W. D. Connolly and K. H. Johnson, MIT Solid State and Molecular Theory Group Report No. 72, page 19 (1970) (unpublished), and private communication.
 10. M. G. Ramchandani, J. Phys. C, Solid State Phys. 3, S1 (1970).
 11. M. G. Ramchandani, J. Phys. F, Metal Phys. 1, 109 (1970).
 12. S. Kupratakuln, J. Phys. C, Solid State Phys. 2, S109 (1970).
 13. L. Hodges, H. Ehrenreich, and N. D. Lang, Phys. Rev. 152, 505 (1966).
 14. H. Ehrenreich and L. Hodges, in Methods in Computational Physics, ed. by B. Alder, S. Fernbach, and M. Rotenberg (Academic Press, New York, 1968), Vol. 8, p. 149.

15. D. E. Eastman and J. K. Cashion, Phys. Rev. Letters 24, 310 (1970).
16. D. E. Eastman, Phys. Rev. Letters 26, 1108 (1971).
17. Because the d electrons' wave functions may have different radial dependences from the bottom of the top of the band, the transition matrix element of \vec{r} , and hence the photoemission cross section, could vary across the band.

Table I. Comparison of Gold d-band Parameters

Description	ΔE_B (eV) ^a	ΔE_d (eV) ^b	$E_F - E_d$ (eV) ^c	Ref.
KKR	0.79	5.25 ^d (5.18)	1.89 ^d (1.93)	9
RAPW	0.54	5.54 (5.58)	1.56 (1.41)	10
RAPW	0.78	4.90 (4.92)	2.21 (2.20)	12
RAPW	0.85	5.07 (5.12)	2.17 (2.04)	8
Interpolation	0.92	5.67 (5.64)	2.34 (2.18)	6
Experiment	--	5.24	2.04	This work

^aFWHM of Poisson broadening function by which theoretical band-structure histogram were multiplied.

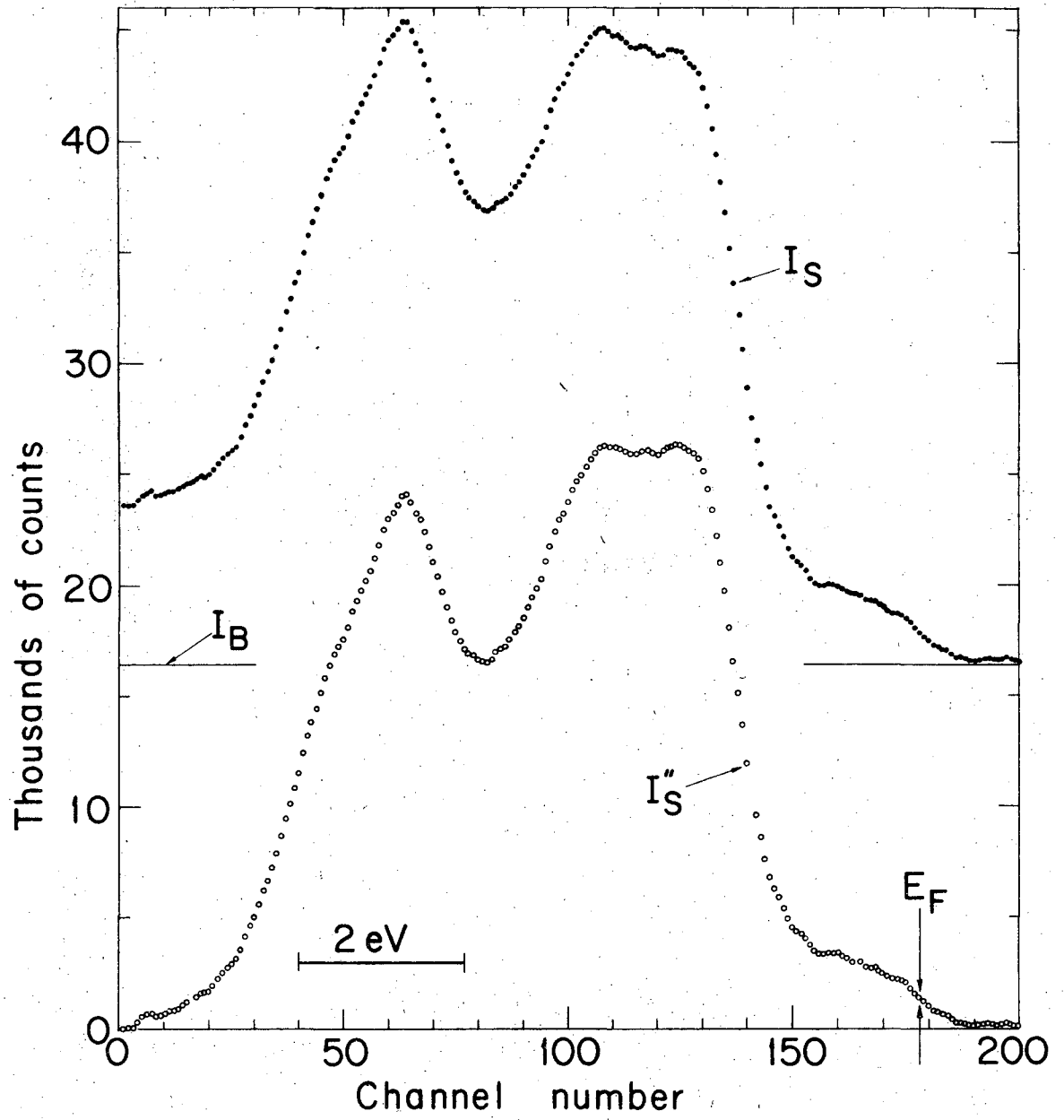
^bFWHM of d band.

^cEnergy difference from Fermi level to a point half way up the higher-energy d-band peak.

^dValues in parentheses were taken from smoothed curves. Values without parentheses were evaluated before smoothing. Accuracy is 0.1 eV.

FIGURE CAPTIONS

- Fig. 1. X-ray photoemission spectrum of the gold valence bands before and after corrections for background and scattering.
- Fig. 2. Comparison of I_S'' with broadened density-of-states function $\rho(E)$ from the relativistic KKR band-structure calculation of Connolly and Johnson (Ref. 9).
- Fig. 3. Comparison of I_S'' with broadened density-of-states function $\rho(E)$ from the relativistic APW band-structure calculation of Ramchandani (Ref. 10).
- Fig. 4. Comparison of I_S'' with broadened density-of-states function $\rho(E)$ from the relativistic APW band-structure calculation of Kupratakuln (Ref. 12).
- Fig. 5. Comparison of I_S'' with broadened density-of-states function $\rho(E)$ from the relativistic APW band-structure calculation of Christensen and Seraphin (Ref. 8).
- Fig. 6. Comparison of I_S'' with broadened density-of-states function $\rho(E)$ from the interpolated band structure calculation by Smith and Traum (Ref. 6).



XBL7111-4853

Fig. 1

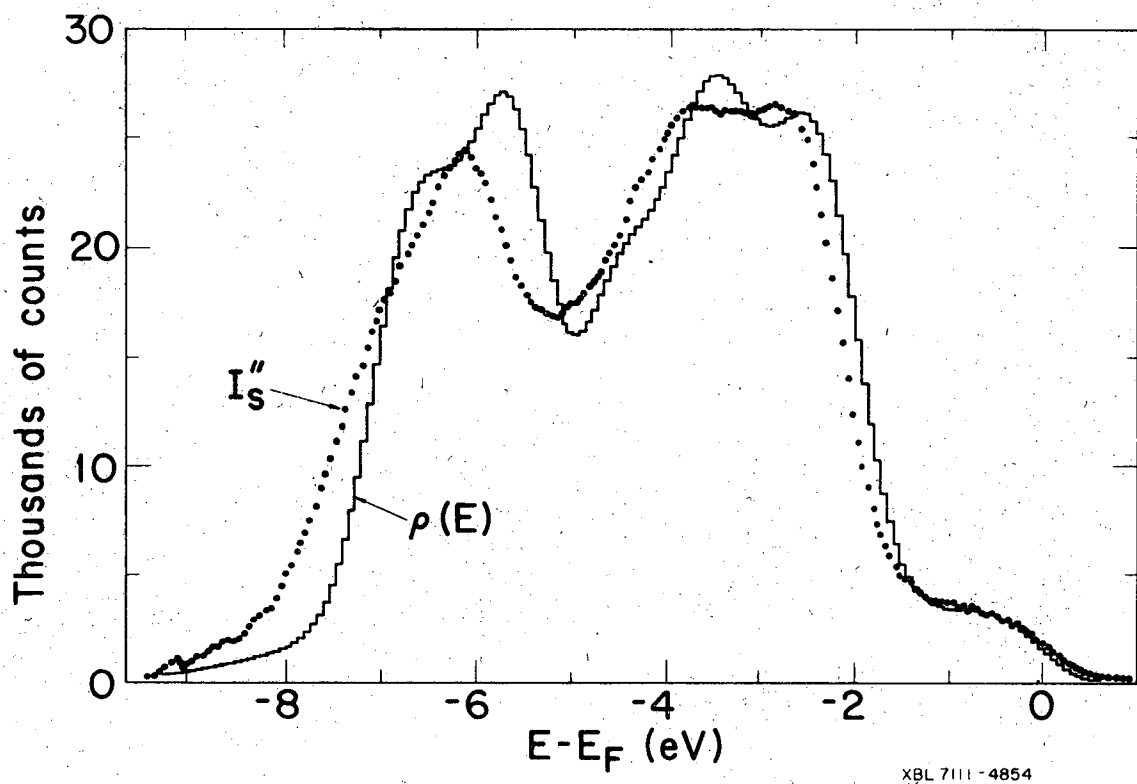


Fig. 2

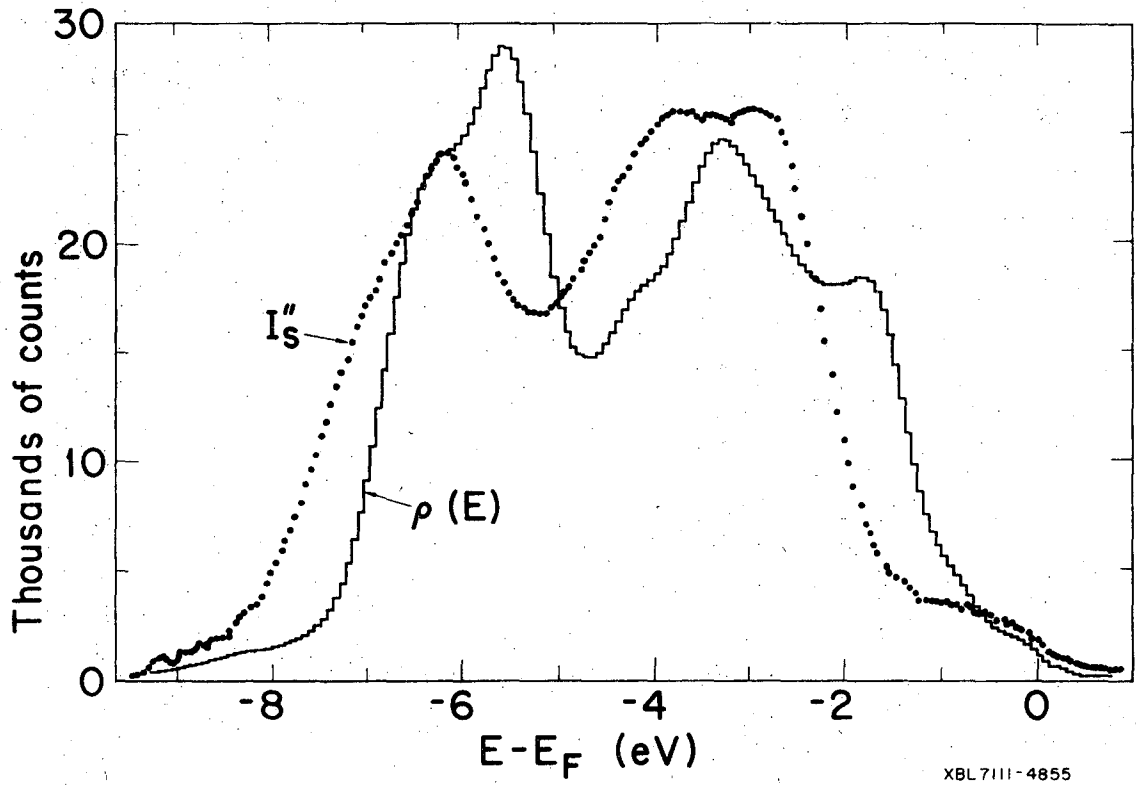


Fig. 3

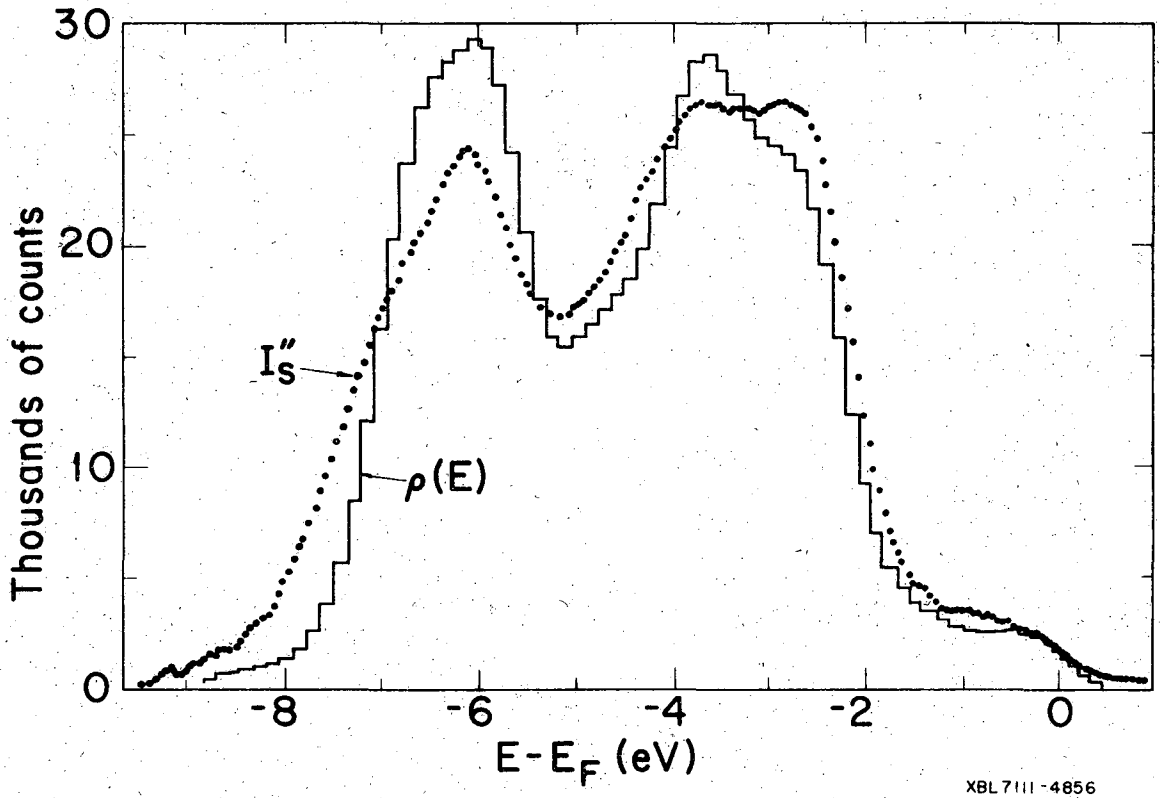
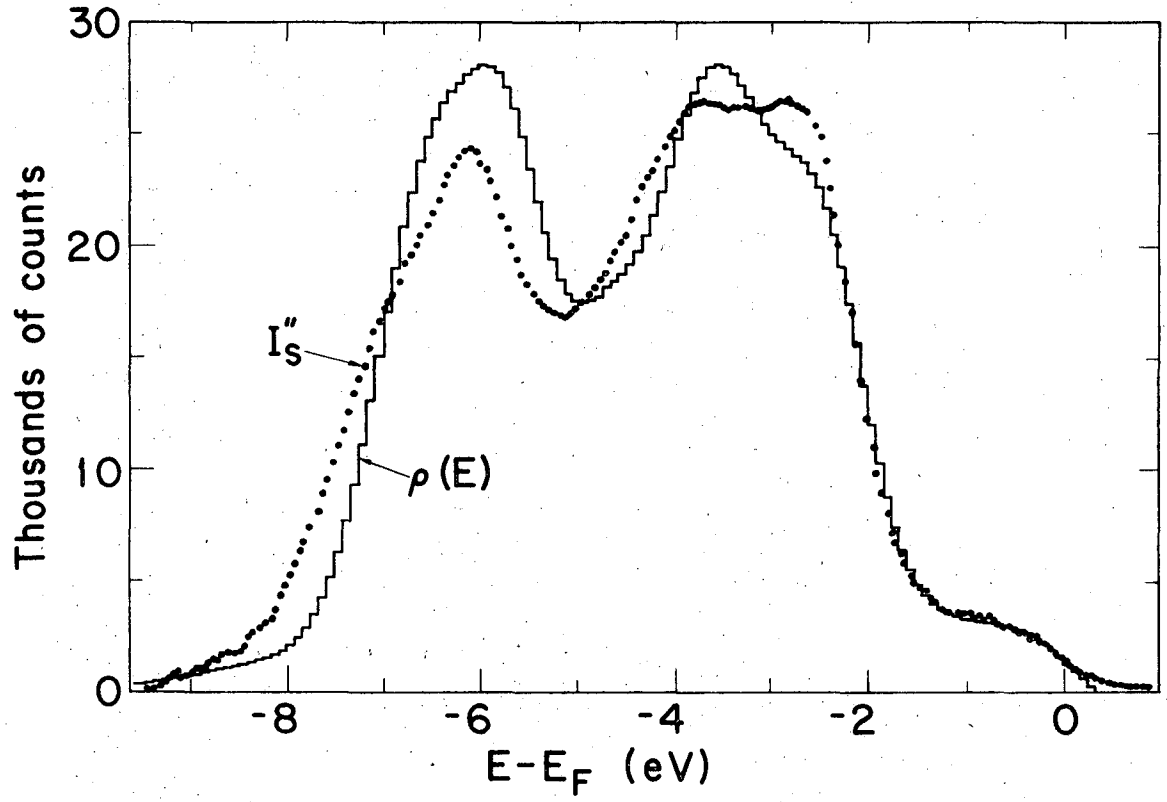
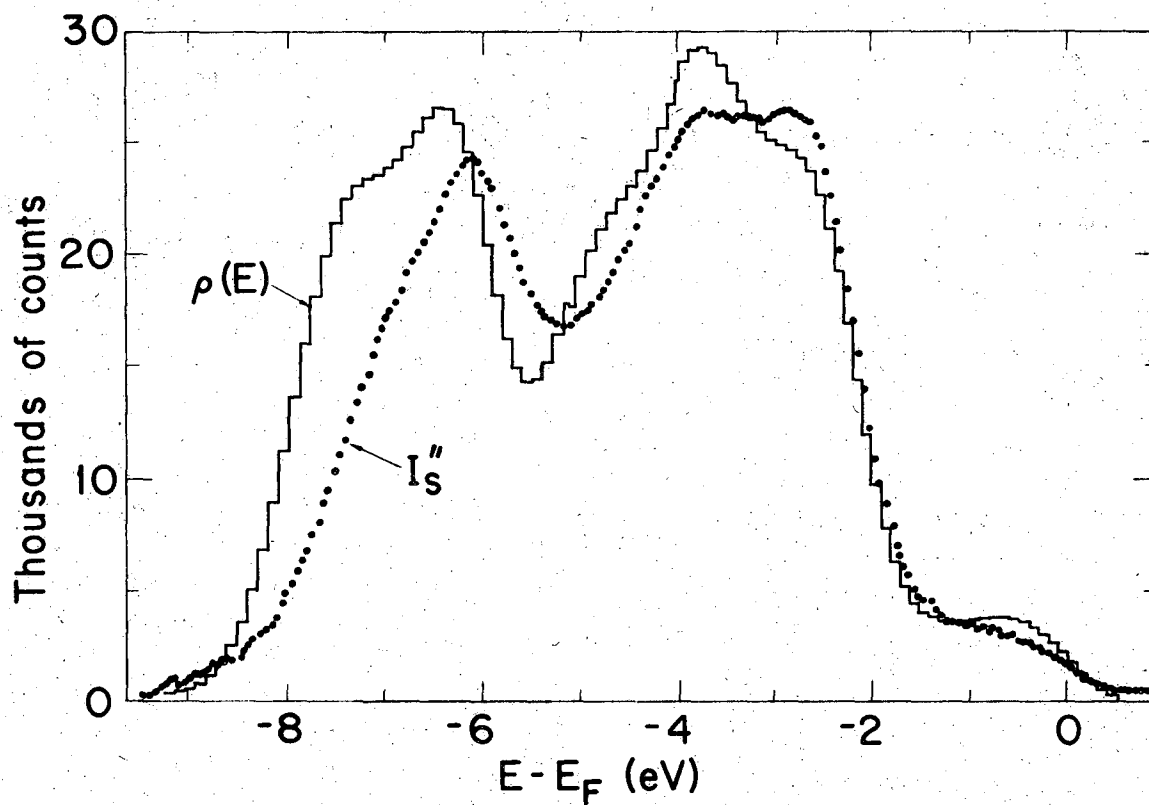


Fig. 4



XBL 7111-4857

Fig. 5



XBL 7111-4858

Fig. 6

LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

TECHNICAL INFORMATION DIVISION
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720