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August, 1978

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MAPPING OF CONDUCTION BANDS IN GaAs BY ANGLE-RESOLVED PHOTOEMISSION*

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Abstract:

Using angle-resolved photoemission spectra in the photon energy range $12 \leqslant h\nu \leqslant 20$ eV, we have mapped selected conduction bands for the (110) direction in GaAs using a simple direct-transition analysis. At higher energies the spectra suggest a one-dimensional density of states interpretation. The two mechanisms are discussed.

Photoelectron spectroscopy has proven to be of great utility in the study of the electronic properties of solids. Recently, angle-resolved photoemission (ARP), together with the direct-transition model, has become well-established as a method for elucidating the band structures of metals.[1] In the case of semiconductors, however, the detailed relationship of the PES spectra and the band structure is much less well understood, and until now most studies of such materials have focused on the elucidation of their integrated densities of states,[2] surface states,[3,4] and interactions with metallic, semi-conducting, or insulating overlayer materials.[5] The interpretation of ARP data for three dimensional solids such as zincblende and rock-salt structure conductors has primarily involved two opposing view-points: the one dimensional density of states (ODDOS) approach and the direction transition model (DTM). Grandke, et al.[6] analyzed spectra at 21.2 eV photon energy for PbS using the former approach, and concluded that it explained the features observed; more recently, Thiry, et al.[7] have studied PbSe for variable photon energies, and have shown the viability of the ODDOS approach for mapping bulk bands. On the other hand, Rogers and Fong[8] used the DTM successfully to interpret GaAs (110) photoemission results for $h\nu \leqslant 8$ eV, and Knapp, et al.[9] have reported using the DTM to 16 eV for this material. Because of the relative complexity of the final-state band structure, however, it has until now been difficult to use ARP data, in an analytical sense, as a probe of the bulk electronic structures of semiconductors; that is, using the spectra to derive, or at least to adjust, dispersion relations,

rather than simply using a theoretical band structure to explain the spectra. In this Communication, we shall present conduction bands for GaAs(110), which were derived by a rather simple analysis. We also present evidence for the ODDOS mechanism at higher photon energies.

The (110) cleavage face of GaAs was chosen for these studies, as its valence band structure is well known,[10-13] and it has been extensively characterized by other methods. Spectra were taken at photon energies up to 28 eV using synchrotron radiation from the SPEAR storage ring at Stanford Synchrotron Radiation Laboratory, using a cylindrical mirror analyzer modified for angle-resolved studies, with an energy resolution of 0.07 eV. The sample was an n-type GaAs(110) crystal cleaved in situ, and mounted on a manipulator that allowed full polar (Θ) and azimuthal (ϕ) rotations; the base pressure was in the 10^{-10} torr range. Spectra were taken for several combinations of Θ and ϕ; the results presented here are for normal emission ($\Theta = 0$), with azimuthal orientations corresponding to the [001] ($\phi = 0°$) and [110] ($\phi = 90°$) directions in the bulk Brillouin zone being in the plane of the polarization vector. The detector lay in the plane of the polarization vector, at a fixed angle of 145° relative to the photon beam. Spectra were taken for two separate samples, and were reproducible; angular alignment was achieved using a He-Ne laser. All binding energies are referenced to the experimental valence band maximum at Γ, taken from the high energy spectra; the spectra were aligned to a constant fermi level as determined from a gold foil in electrical contact with the sample.

In Fig. 1 we present spectra in the photon energy range 12-20 eV, for both azimuthal orientations. As shown by Lapeyre and coworkers,[13] the polarized nature of the incident radiation determines selection rules for the spectra. In this case, only Σ_1 final states are allowed for normal emission, and the orientation of the polarization vector relative to the sample mirror plane implies that for $\phi = 90°$, all initial states are allowed, while for $\phi = 0°$, the highest valence band A (we label the 3 highest initial state bands A-C, in order of increasing binding energy), of Σ_2 symmetry, will not be observed. All the features in the spectra seem to be bulk-like, except for the shoulder at 0.8 eV binding energy (BE) for $h\nu = 12$ eV. This peak is also observed at 0.6 eV BE for $h\nu = 9$ eV, and at 0.7 eV BE for $h\nu = 7$ eV; in the latter two cases, no direct transitions are predicted within 1 eV of this BE, and we accordingly assign the feature as a surface state. While a surface state is not predicted at Γ,[12] the finite angular resolution of the analyzer would allow the observation of surface states nearby.

We have chosen to analyze these spectra by using them to map the allowed final states. The valence bands given by Chelikowsky[10] were chosen, as his C band BE along the K-X direction was in better agreement with our data than that of Pandey and Phillips[11] (PP). Our procedure was essentially as follows. By comparing the PP band structure with a free electron band structure, it was possible as a first approximation to assign a projection of the group velocity along the [110] direction for each of the conduction bands. We note that, for most of the real bands, several free-electron bands will be dominant, one in each segment

through the Brillouin zone, because the bands admix and invert several times in going from Γ to X; this was taken into account. Most of the final state bands under consideration arose from five G vectors and their associated energy-degenerate partners: (220), $(1\bar{1}1)$, $(\bar{1}\bar{1}\bar{1})$, $(0\bar{2}0)$, and $(02\bar{2})$; all of these free electron bands have [110] projections of 60% or greater. The remaining PP final states had associated projections of 1/3 or less and were therefore disallowed because of the angle-resolved nature of the experiment. Using this selected group of PP final states, the energies of all possible direct transitions were calculated. By comparing these assignments to the spectra, it was possible to unambiguously assign empirical transition energies to roughly 50% of the transitions. These energies were then used to map the accessible final state bands; finally, these empirical bands were then used to predict the balance of the transitions. All peaks were accounted for in this manner.

Such an approach is iterative, and its success depends on starting with a rather good idea of the final-state band structure. We emphasize that our analysis was conservative, and only relatively small adjustments were made in the final-state bands. Where several transitions occurred under a single peak, no empirical energy was incorporated into the conduction band structure unless additional analysis, such as following trends in given initial to final-state transitions, gave a way of making an unambiguous assignment. In a few cases, bands with the proper [110] projection were not observed; this was attributable either to the photon energy range employed or masking of the associated transition

by other features. Consistency was maintained at all times; in particular, a transition from a given initial state to a given (k) region of a final state was assigned for all photon energies where it was predicted theoretically, unless it was clearly associated with a peak that grew in or out with increasing photon energy. For a very few transitions, which fell in gaps in the spectra, it was necessary to assume that they were disallowed due to cross-section effects; again, such transitions were discarded in all spectra to ensure consistency. Polarization effects were also utilized whenever possible, and in particular it was possible by calculating difference spectra to assign some A band transitions in the $\phi = 90°$ spectra.

The results of this mapping are shown in Figure 2, where they are compared to the theoretical band structure of PP. We have shifted the PP bands down by 0.5 eV to give the best overall agreement, and in fact this shift is necessary if the PP final state bands are to predict all the major features in the spectra. We note that one Σ_2 final state band is observed (band 2). This arises from the finite angular resolution of the spectrometer, coupled with the fact that this band has a deep minimum, and concomitant high density of states, midway along the Γ-K line. The associated peaks are at 3.7, 4.4, and 5.2 eV BE for photon energies of 12, 13, and 14 eV, respectively, and correspond to transitions from the C initial state. The peak at 4.4 eV for $h\nu$ = 14 eV comes from the minimum in band B near K, and indicates that the theoretical initial state band structure is in error here by roughly

0.2 eV; no attempt was made to correct for this in our analysis. Broadening due to the finite mean free path may be estimated; for an escape depth[14] of 15 Å, the k broadening is roughly 1/16 of the Γ-X distance.[15] The final energy uncertainty depends in each case on the nature and shape of the peak involved, but we estimate it at ±0.2 eV in most cases; of course, any errors in the initial state band structure will also contribute.

Figure 3 shows the evolution of the ARP spectra for higher photon energies, $h\nu$ = 22-28 eV. Only the $\phi = 90°$ spectra are shown: those for $\phi = 0°$ were similar. Without a theoretical final state band structure we are unable to present to make a quantitative interpretation of these spectra. It seems evident, however, that a new photoemission mechanism is becoming dominant in this energy range. We note in particular that the spectra are still evolving up to $h\nu \cong 25$ eV, but that they have settled for higher energies into a structure that does not vary markedly with photon energy.

The most probable explanation for this behavior is the onset of a ODDOS regime. At electron kinetic energies somewhat above the plasmon threshold, electron mean free paths fall to very low values in metals and semiconductors. In fact Pianetta[16] found an electron mean free path in GaAs of 6 ± 1.5 Å at 40 eV kinetic energy. This would imply that our highest energy spectra are dominated by the first two GaAs atomic layers. Moreover, the consequent broadening in $k_\perp$ implies effective non-conservation of this quantum number and sampling through the entire Brillouin zone in a direction normal to the surface:

i.e., a ODDOS sampling. We note that Thiry, et al.[7] have observed ODDOS behavior in PbSe at $h\nu$ = 35 eV photon energy and have tentatively interpreted it in this way, using the ODDOS to identify the critical points and map the valence band structure. To test this interpretation for the GaAs case, we have computed the ODDOS for GaAs along ΓKX and compared it with our high-energy spectra in Figure 4. The agreement is excellent, especially when we note that the s to p photoemission cross section ratio is very small at these energies, effectively suppressing the more tightly bound bands. Thus, the evidence is strong that a transition occurs between $h\nu$ = 20 eV and $h\nu$ = 30 eV from the direct transition mechanism to ODDOS behavior in photoemission from GaAs.

Two caveats are necessary, both of a generic nature and not specific to GaAs. First, a strictly logical approach would require that the direct-transition model be shown incapable of interpreting the high-energy spectra. This would be difficult in general as the final state bands become more numerous at high energies, and it is not possible at this time because we do not have theoretical high-energy bands. It is very unlikely that our high-energy spectra can be reconciled with the DTM. The second caveat is simply that the transition from the DTM to ODDOS behavior with photon energy is not perfectly sharp, and one may expect some evidence of both at higher and lower energies. It is an obvious, but often neglected, fact that ARP spectra usually contain some spectral area that is not accounted for by the photoemission mechanism that dominates the spectra.

In conclusion, we have shown that it is possible by a simple analysis to map selected conduction bands in GaAs using ARP in the photon energy regime where the DTM is valid. For higher photon energies, the ODDOS is seen to account for the observed spectral features. It seems likely that such a two regime approach will account for the ARP spectra of other semiconductors as well, and that it should be possible to understand photoemission from three dimensional solids in this framework.

REFERENCES

*This work was performed at the Stanford Synchrotron Radiation Laboratory, which is supported by the NSF Grant No. DMR 73-07692 A02, in cooperation with the Stanford Linear Accelerator Center and was done with support from the Division of Chemical Sciences, Office of Basic Energy Sciences, U. S. Department of Energy.

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1. There are many references pertaining to direct transitions in ARP in metals. For example, G. V. Hansson and S. A. Flodström, Phys. Rev. B17, 473 (1978) have studied silver in detail for $h\nu < 11.6$ eV, while J. Stöhr, P. S. Wehner, R. S. Williams, G. Apai, and D. A. Shirley, Phys. Rev. B17, 587 (1978) have studied Cu(110) up to $h\nu = 160$ eV.

2. L. Ley, R. A. Pollak, F. R. McFeely, S. P. Kowalczyk, and D. A. Shirley, Phys. Rev. B9, 600 (1974); D. E. Eastman, W. D. Grobman, J. L. Freeouf, and M. Erbudak, Phys. Rev. B9, 3473 (1974).

3. J. A. Knapp and G. J. Lapeyre, J. Vac. Sci. Tech. 13, 757 (1976).

4. G. P. Williams, R. J. Smith, and G. J. Lapeyre, private communication.

5. P. E. Gregory and W. E. Spicer, Phys. Rev. B12, 2370 (1975); W. E. Spicer, P. Pianetta, I. Lindau, and P. W. Chye, J. Vac. Sci. Tech. 14, 885 (1977); P. Perfetti, D. A. Denley, K. A. Mills and D. A. Shirley, App. Phys. Lett. in press.

6. T. Grandke, L. Ley, and M. Cardona, Phys. Rev. Lett. 38, 1033 (1977).

7. P. Thiry, R. Pinchaux, G. Martinez, Y. Petroff, J. Lecante, J. Paigne, Y. Ballu, C. Guillot, and D. Spanjaard, private communication.

8. D. L. Rogers and C. Y. Fong, Phys. Rev. Lett. 34, 660 (1975).

9. J. A. Knapp, D. E. Eastman, K. C. Pandey, and F. Patella, Bull. APS 23, 399 (1978).

10. J. R. Chelikowsky, Ph.D. Thesis, LBL-3962 (1975).

11. See Ref. 13 for the Γ-K-X band structure; the original calculations are in K. C. Pandey and J. C. Phillips, Phys. Rev. B9, 1552 (1974), loc. cit., 1560.

12. D. J. Chadi, Phys. Rev. B, in press.

13. J. A. Knapp and G. J. Lapeyre, Il Nuovo Cim. 39B, 693 (1977).

14. W. E. Spicer, J. S. Johannessen, and Y. E. Strausser, Varian Report VR-98, pg. 14; I. Lindau and W. E. Spicer, J. Elect. Spect. 3, 409 (1974).

15. D. J. Spanjaard, D. W. Jepsen, and P. M. Marcus, Phys. Rev. B15, 1728 (1977).

16. Piero A. Pianetta, Ph.D. Thesis, Stanford University, 1977. Stanford Synchrotron Radiation Laboratory Report 77/17, page 127.

FIGURE CAPTIONS

Fig. 1. Spectra in the photon energy range 12-20 eV for normal emission and both azimuthal orientations.

Fig. 2. Empirical and theoretical conduction bands for GaAs (110). Portions of bands 5, 6, and 7 are not observed for the reasons discussed in the text. Dashed lines indicate a (110) projection of less than 1/3 for the group velocity.

Fig. 3. Spectra at normal emission for the photon energy range 22-28 eV.

Fig. 4. ODDOS compared to spectra at 26 and 28 eV photon energy. Note that the ODDOS should be broadened and corrected for cross section effects to allow a direct comparison with experiment.

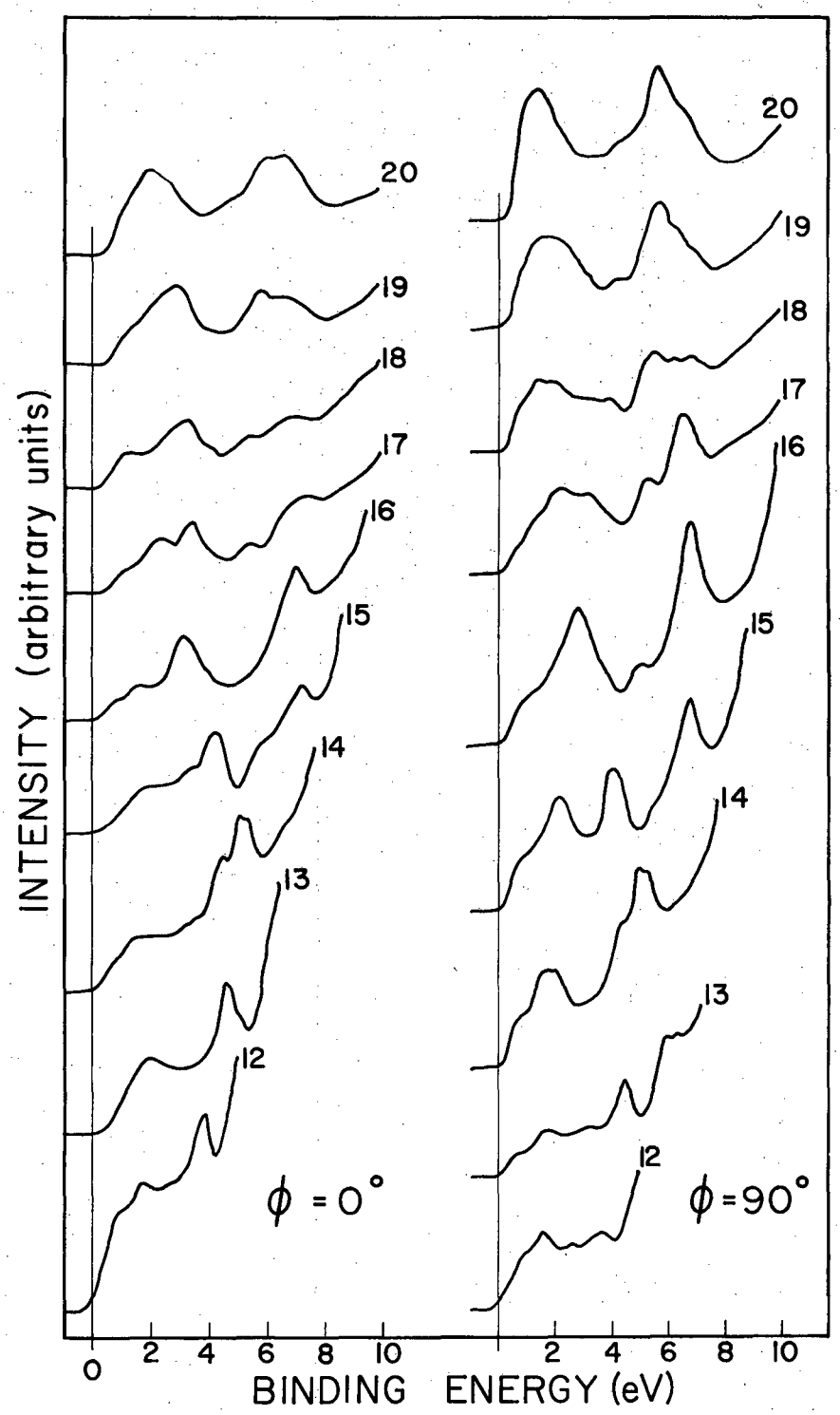

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Fig. 1

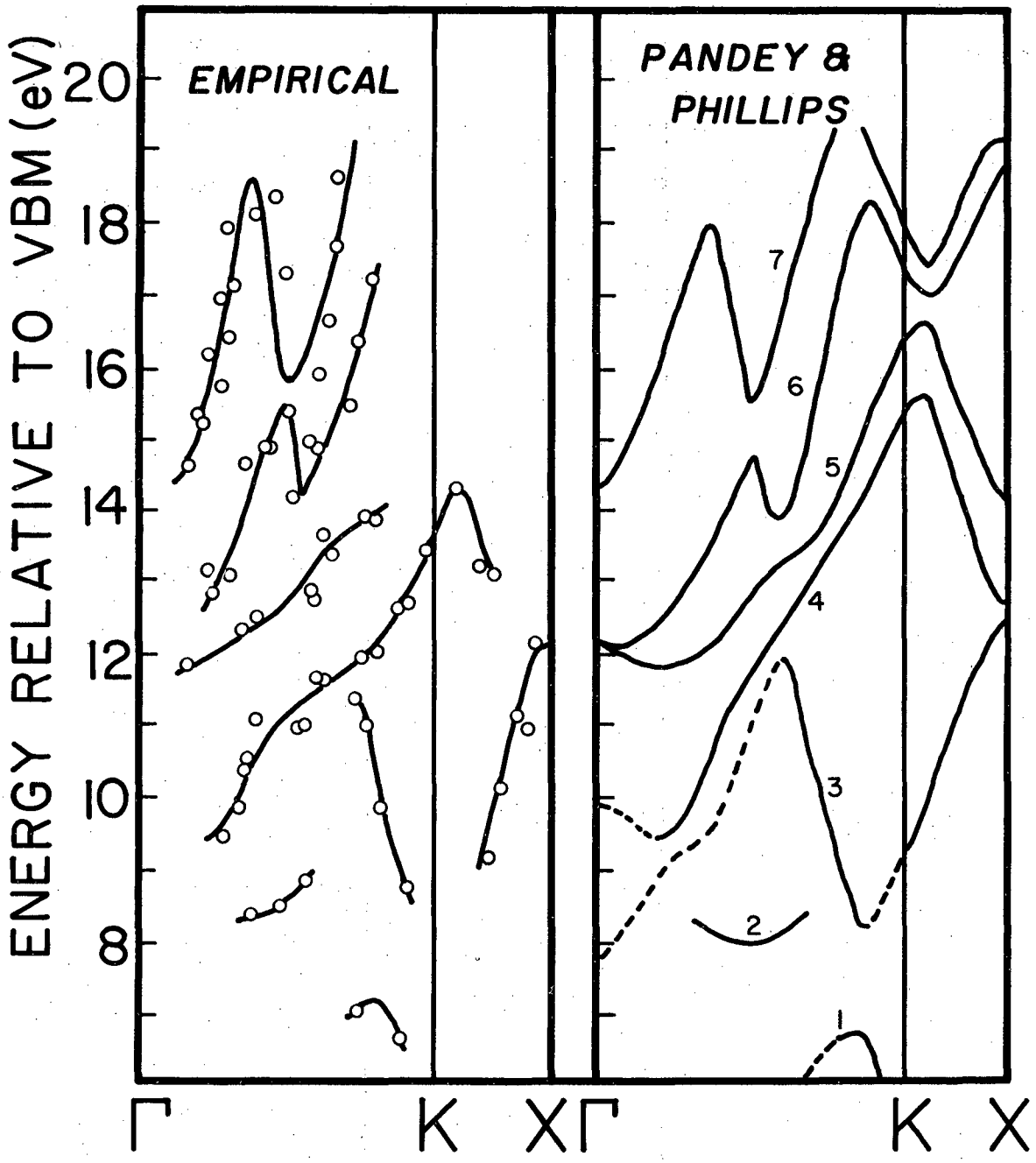

Fig. 2

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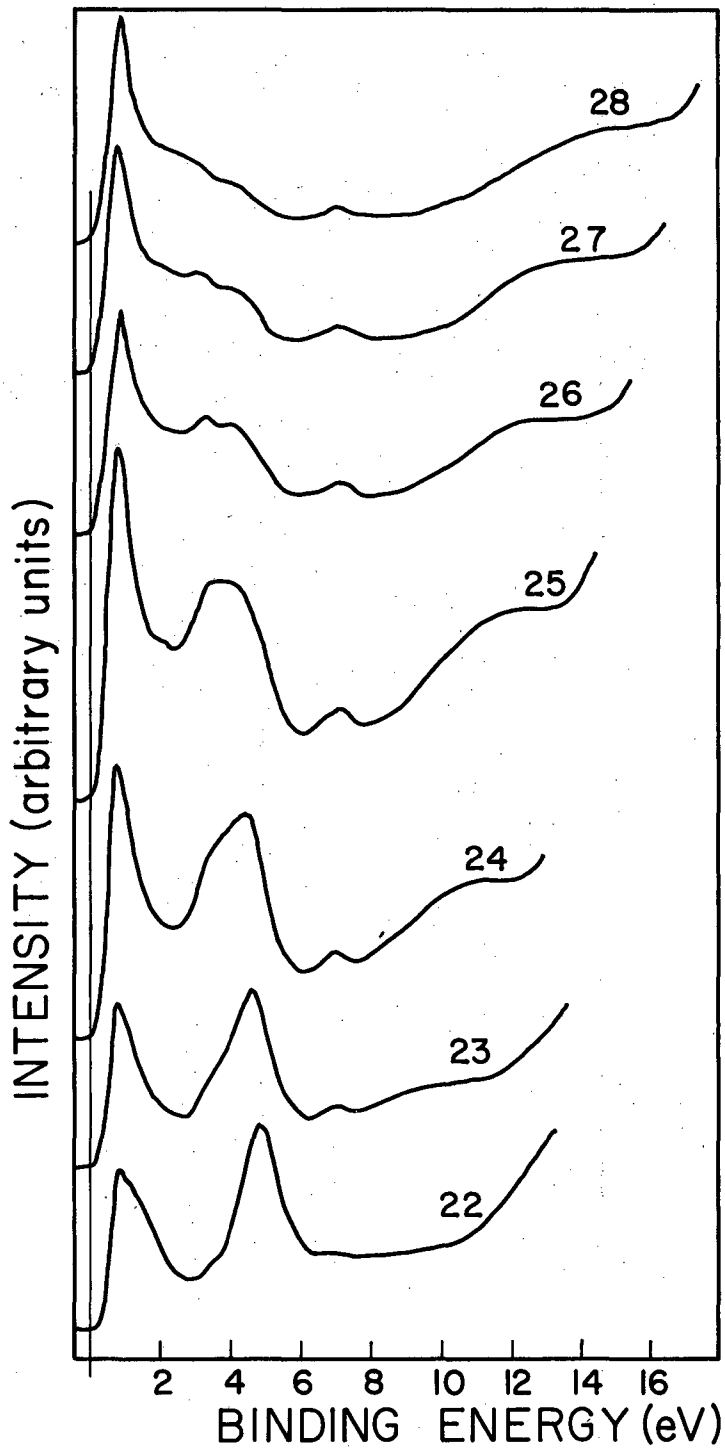

Fig. 3

XBL 787-9771

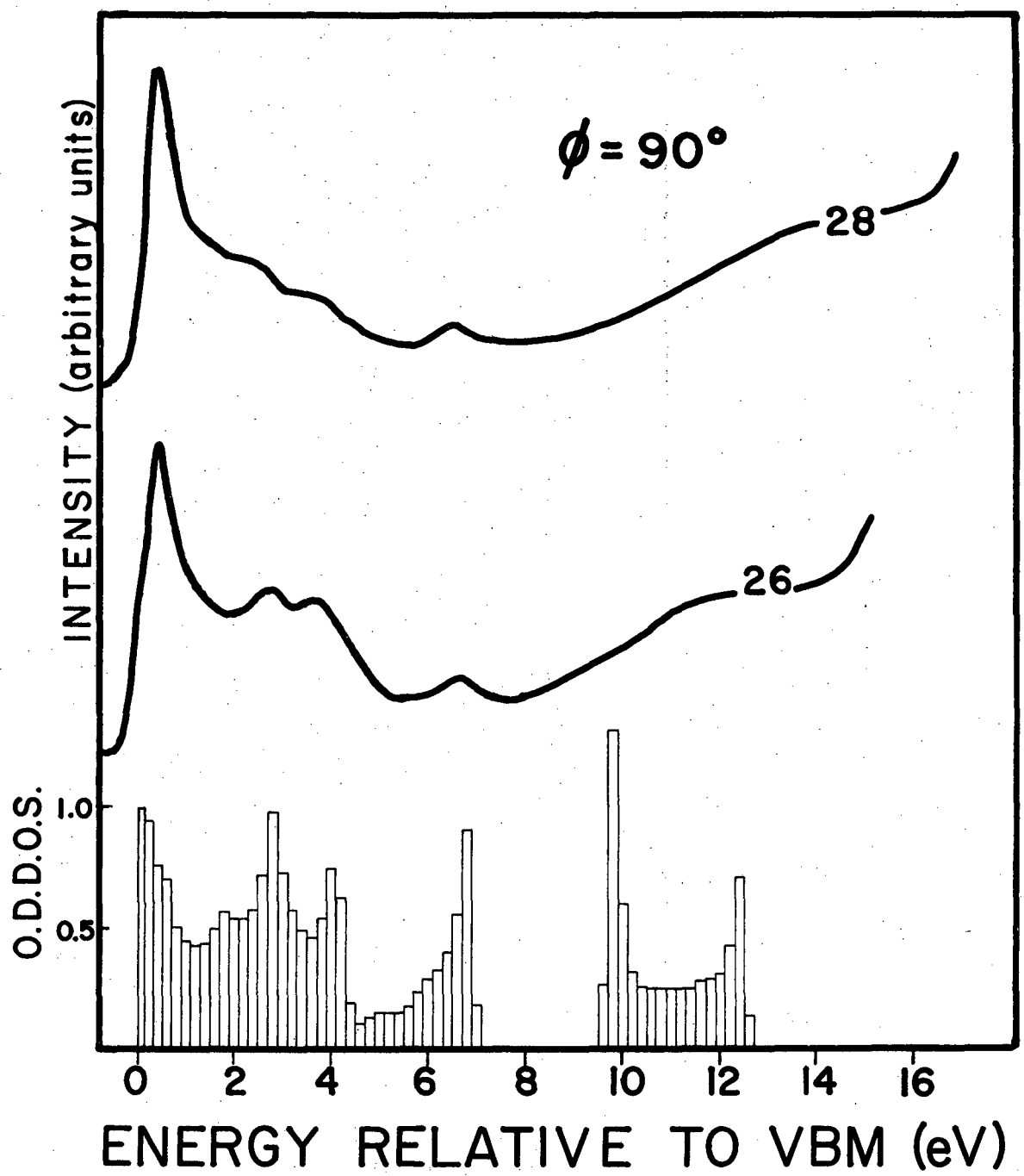

Fig. 4

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This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

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