Lawrence Berkeley National Laboratory
Recent Work

Title
ELLIPSOMETRY OF MASS-TRANSPORT BOUNDARY LAYERS

Permalink
https://escholarship.org/uc/item/8r68r6xt

Author
Muller, Rolf H.

Publication Date
1975-09-01

eScholarship.org Powered by the California Digital Library
University of California

U U U U 4 3 0 5 5 7 0

Presented at the 3rd International Conference
on Ellipsometry, University of Nebraska,
Lincoln, NB, September 23 - 25, 1975

LBL-3929
c.1

RECEIVED
LAWRENCE
BERKELEY LABORATORY

NOV 5 1975

LIBRARY AND
DOCUMENTS SECTION

ELLIPSOMETRY OF MASS-TRANSPORT BOUNDARY LAYERS

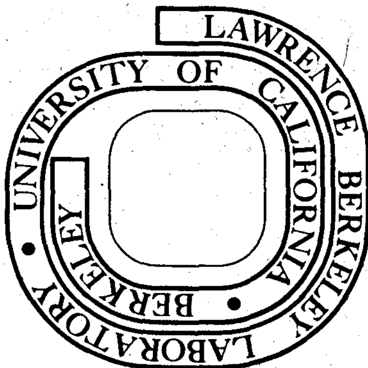
Rolf H. Muller and Craig G. Smith

September 1975

Prepared for the U. S. Energy Research and
Development Administration under Contract W-7405-ENG-48

For Reference

Not to be taken from this room



LBL-3929
c.1

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.

0 0 0 0 4 3 0 5 5 7 1

3rd International Conference on Ellipsometry, September 23-25, 1975, University of Nebraska

LBL-3929

ELLIPSOMETRY OF MASS-TRANSPORT BOUNDARY LAYERS

Rolf H. Muller and Craig G. Smith

Inorganic Materials Research Division, Lawrence Berkeley Laboratory and Department of Chemical Engineering; University of California Berkeley, California 94720

ABSTRACT

The effect of mass-transport boundary layers, that are often associated with surface reactions proceeding at high rates, on ellipsometer measurements of the underlying surface has been investigated for typical transport conditions in liquids. The effect can be of significant extent and depends primarily on concentration difference across the boundary layer, angle of incidence and optical constants of the surface. A simplified method for predicting boundary-layer effects based on light refraction is introduced. Computations are in good agreement with experiments.

INTRODUCTION

Heterogeneous reactions on solid surfaces are generally accompanied by the formation of a mass-transport boundary layer, i.e., a region near the interface where the concentration of the reacting species in the fluid phase is different from that in the bulk fluid. In contrast to the conventional ellipsometry of static or slowly-changing surfaces, it can be expected that the observation of fast-changing surfaces with automatic ellipsometers involves mass-transport (or diffusion) layers that have a significant optical effect. This work was undertaken to develop techniques to account for the effect of mass-transport boundary layers on the ellipsometric observation of surfaces, to establish this effect for typical electrochemical reactions and to explore the use of ellipsometry for the measurement of boundary layers, particularly those that are too thin for observation by interferometry.[1]

0 0 0 0 4 3 0 5 5 7 2

THEORY AND COMPUTATIONS

Mass-transport boundary layers are optically inhomogeneous, with the refractive index varying continuously from the (homogeneous) bulk fluid to the interface. The refractive index may increase or decrease toward the interface according to different functional relationships.

Experimentally, boundary layers have been generated by the electrochemical (anodic) dissolution or (cathodic) deposition of copper under different convection conditions. A linear function has been used to relate refractive index, n, with concentration C (M $CuSO_4$) at 546.1 nm wavelength

$$n = 1.3345 + 0.029C \quad .$$

Although aqueous copper sulfate solutions are colored, the optical computations are not perceptively affected by the very weak light absorption. The imaginary part of the refractive index ($k = 1.8\times10^{-6}$ Ref 2,3) has, therefore, been neglected.

Computations have been conducted for linear and parabolic functions of the refractive index with distance y from the interface. Such concentration profiles are approximations to convective boundary layers[4] with interfacial index n_i and bulk fluid n_b.

$$n = n_i + \frac{n_b - n_i}{\delta} y$$

$$n = n_i + (n_b - n_i) \left[1 - \left(1 - \frac{y}{\delta}\right)^2\right] \quad .$$

The multiple-film method[5] of computation with up to 400 layers has been used. Figure 1 shows the dependence of the relative phase Δ on the film thickness δ, for cathodic deposition with the interfacial concentration

c_i held constant (potentiostatic mode). The figure illustrates two surprising results, (1) for transport regions greater than about 10μ Δ is independent of thickness but depends only on the concentration difference between bulk and interface, (2) Δ is not greatly affected by the nature of the concentration profile. The figure also illustrates that mass-transport boundary layers can change the ellipsometer parameter Δ by several degrees, an amount often not negligible in ellipsometer measurements. The change in the ellipsometer parameter ψ is usually found to be smaller than that in Δ, but it follows a similar thickness dependence. For an anodic-dissolution boundary layer, the changes in Δ and ψ are of opposite sign but the same magnitude as those for the cathodic deposition.

The independence of ellipsometric parameters upon film thickness in the thick-film limit is most unusual, since the values of Δ and ψ for a homogeneous transparent film show an unabated periodic behavior with increasing film thickness. Computed reflection coefficients from the interior of the inhomogeneous film show that the principal reason for this behavior is the light deflection (refraction) in the film: At large boundary layer thicknesses, the refractive-index gradient is small enough to allow light to be deflected without attenuation by reflection, while at small thicknesses (large gradients), reflection occurs simultaneously with refraction. In the thick-film limit, the effect of the boundary layer is solely to change the angle of incidence of the light upon the substrate. This change depends only on the refractive indices (concentrations) in the bulk fluid and at the interface, and can easily be determined by use of Snell's law of refraction. The validity of this approach to computing the optical effect of boundary layers is illustrated in Table I. For a 5μ thick layer the light-deflection

0 0 0 0 4 3 0 5 5 7 3

model approximates the much more involved inhomogeneous film-computation quite well, while agreement up to the third decimal place is found for a 500μ thick layer.

It would seem very desirable to represent the inhomogeneous boundary layer by an optically equivalent homogeneous film. This is, however, not possible over any significant range of thickness, because the thickness dependence illustrated in Fig. 1 differs from that for homogeneous films. When the refractive index decreases toward the interface, total reflection in the boundary layer is possible. The ellipsometer measurements are then independent of the substrate. Some limiting concentration-differences necessary for total reflection under different angles of incidence are listed in Table II.

The change $\delta\psi$ and $\delta\Delta$ in ellipsometer parameters ψ and Δ, defined positive for an increase due to mass-transport boundary layers, depends on the angle of incidence, ϕ. Computations for the thick-film limit, with different substrate optical constants n_{cs}, are shown in Fig. 2. The data relate to the slope of the dependence of ψ and Δ on the angle of incidence. As illustrated in Fig. 3, the effect of boundary layers, under most conditions, is proportional to the concentration difference $\delta n_i = n_b - n_i$ across the layer.

Figures 4 and 5 allow an experimenter to estimate errors in ellipsometer measurements caused by mass-transfer boundary layers with substrates of arbitrary optical constants. The errors are largest for substrates with large real parts and rather small imaginary parts of the refractive index.

Neglecting the effect of mass-transfer boundary layers can lead to errors in the quantities derived from ellipsometer measurements,

such as film thicknesses or optical constants of films or substrates.

The magnitude of such errors has to be determined for each individual case. An example from our work on the formation of cuprous oxide during the anodic dissolution of copper is illustrated in Fig. 6: ψ and Δ values computed for oxide layers up to 200Å thickness are parallel-displaced by the presence of a boundary layer. For a 0.4M concentration difference and no oxide present, erroneous substrate optical constants of 1.03-2.60i (compared to the real 0.94-2.24i) would be derived from the measurement. The shift in Δ is of similar magnitude as that due to a change in oxide thickness by 100Å. With the same boundary layer, a 100Å thick oxide layer appears to possess a refractive index of 2.10-1.77i compared to the true value of 2.06-1.55i. With the true optical constants for film and substrate, a film thickness could not be derived from the measurement.

0 0 0 0 4 3 0 5 5 7 4

EXPERIMENTS

Experimental observations of the effect of boundary layers on ellipsometer measurements have been made for comparison to theoretical predictions. Boundary layers have been generated by the electrochemical deposition or dissolution of copper under different convective conditions, with the measurements being conducted with our automatic ellipsometer.[6] Electrodes of 1×3 cm active surface have been used in an electrolytic cell or flow channel of trapezoidal cross section; the angle of incidence was 75°.

An experimental difficulty arises due to changes in the optical properties of the metal during the experiments. We have been able to significantly reduce roughening of the electrode surface, the principal cause of surface changes during dissolution and deposition, by use of densely-packed faces (111 and 100) of copper single-crystals as electrode surfaces. Oxide formation, another cause of surface changes, has been controlled by removing dissolved oxygen from the electrolyte. In addition, we have been able to separate surface and boundary-layer effects in the presence of convection, on the basis of the larger time constant for roughening, by use of interruption techniques. This procedure is illustrated in Fig. 7. A steady state in the effect of the boundary layer is reached in about 5s; the noise in the ellipsometer signal is greatly reduced with the single crystal. Without an oxide film, changes in the surface of the polycrystalline specimen would result in a persistant slope in the base line.

Table III shows a comparison of experimentally observed and theoretically predicted ellipsometer measurements for deposition and dissolution boundary-layers of different thickness and interfacial concentration (determined from flow velocity and current density). It can be seen that under most circumstances, theoretical predictions have been confirmed by experiment, despite the experimental difficulties described and the use of a relatively small electrode that did not cover an entire cell wall to assure uniform current distribution. The major experimental uncertainty was caused by poor control of flow velocity. The experiments confirm the opposite effects of deposition and dissolution boundary-layers, the dependence of the effects on concentration difference and the lack of dependence on boundary-layer thickness.

0 0 0 0 4 3 0 5 5 7 5

CONCLUSIONS

For most transport conditions in liquids the effect of mass-transport boundary layers is sensitive to the refractive index (concentration, temperature) at the interface but not to the thickness of the layer. The magnitude of the effect greatly depends on the angle of incidence and the optical constants of the solid phase. The effect can reach amounts that can significantly alter the interpretation of measurements. Ellipsometry complements the observation of boundary layers by interferometry, where the interfacial refractive index may be difficult to derive precisely from the observations.[7]

ACKNOWLEDGEMENT

This work was conducted under the auspices of the U. S. Energy Research and Development Administration.

REFERENCES

1. F. R. McLarnon, R. H. Muller and C. W. Tobias, Appl. Opt., in press.

2. M. G. Mellon, J. Phys. Chem. 31, 161 (1927).

3. R. Mecke, Z. Phys. Chem. 111, 126 (1929).

4. V. G. Levich, Physicochemical Hydrodynamics (Prentice Hall, Englewood Cliffs, NJ, 1962), pp. 39-138.

5. O. S. Heavens, Optical Properties of Thin Solid Films (Dover, NY, 1956), p. 63.

6. H. J. Mathieu, D. E. McClure and R. H. Muller, Rev. Sci. Instrum. 45, 789 (1974).

7. F. R. McLarnon, R. H. Muller and C. W. Tobias, J. Opt. Soc. Am., in press.

Table I. Validity of light-deflection model for computing the effect of cathodic mass-transport boundary layers with parabolic concentration profiles. Bulk fluid 0.1 M $CuSO_4$, n = 1.3374; substrate Cu, n = 0.94-2.33i.

Interfacial Concentration M $CuSO_4$	Boundary Layer Thickness μ	Angle of Incidence		Computation Based On			
		Macroscopic	At Interface	Inhomogeneous Film		Light Deflection	
		deg	deg	ψ	Δ	ψ	Δ
0.4	0	60	60.00	36.253	107.484	36.253	107.484
0.2	5	60	60.43	36.205	106.496	36.209	106.478
0.0	5	60	60.87	36.158	105.472	36.166	105.434
0.0	500	60	60.87	36.166	105.431	36.166	105.434
0.4	0	75	75.00	37.492	58.058	37.492	58.058
0.2	5	75	75.96	37.747	54.727	37.769	54.671
0.0	5	75	76.99	38.053	51.067	38.104	50.941
0.0	500	75	76.99	38.101	50.937	38.104	50.941

0 0 0 0 4 3 0 5 5 7 6

Table II. Total reflection on cathodic boundary layers with parabolic concentration profile. Bulk fluid 1.0 M $CuSO_4$, n = 1.3635.

Angle of Incidence (Macroscopic) deg	Boundary Layer: Minimum Interfacial Conc. M $CuSO_4$
75	0
79	0.14
81	0.42
83	0.65
85	0.82

Table III. Experimental test of computed changes in ellipsometer parameters Δ and ψ due to the presence of mass-transport boundary layers with different thickness and concentration difference. Electrochemical deposition and dissolution of copper in aqueous copper sulfate, $\phi = 75°$, $\lambda = 546.1$ nm, convective diffusion.

Boundary Layer			Changes in Δ		Changes in ψ	
Nature	Thickness μ	Conc. Difference M $CuSO_4$	Calculated deg	Experimental deg	Calculated deg	Experimental deg
Deposition	50	-0.016	-0.23	-0.30	+0.04	+0.16
	50	-0.096	-1.39	-1.40	+0.18	+0.18
	87	-0.083	-1.25	-1.38	+0.11	+0.14
	26	-0.080	-1.16	-1.16	+0.13	+0.20
	76	-0.094	-1.36	-1.36	+0.17	+0.25
Dissolution	80	0.108	+1.54	+1.67	-0.23	-0.30
	80	0.206	+2.93	+3.02	-0.30	-0.52
	80	0.714	+8.92	+8.50	-0.99	-1.42

0 0 0 0 4 3 0 5 5 7 7

FIGURE CAPTIONS

Fig. 1. Effect of mass-transport boundary layers of thickness δ, resulting from the deposition of Cu from 0.1 M $CuSO_4$, on the ellipsometer parameter Δ. Concentration difference between bulk and interface indicated along curves. ——— parabolic concentration profile, ----, Δ linear concentration profile. Refractive index of substrate 0.94-2.33i.

Fig. 2. Dependence of the change in Δ and ψ due to anodic boundary layer on the angle of incidence ϕ for different substrate optical constants n_{cs}. Thick-film limit, bulk fluid refractive index n_b = 1.3345, refractive-index difference δn_i = 0.03.

Fig. 3. Dependence of the change in Δ and ψ due to anodic boundary layer on the refractive-index difference δn_i for different substrate optical constants n_{cs}. Thick-film limit, bulk fluid refractive index n_b = 1.3345, angle of incidence ϕ = 70°.

Fig. 4. Dependence of the change in Δ due to anodic boundary layer on the substrate refractive index n - ki. Thick-film limit, bulk fluid refractive index n_b = 1.3345.

Fig. 5. Dependence of the change in ψ due to anodic boundary layer on the substrate refractive index n - ki. Thick-film limit, bulk fluid refractive index n_b = 1.3345.

Fig. 6. Effect of mass-transport boundary layer on observation of growing oxide film. Thick-film limit, ΔC is change in $CuSO_4$ from bulk value of 0.1M. Porous Cu_2O of indicated thickness (n = 2.06-1.55i), on Cu (n = 0.94-2.24i).

0 0 0 0 4 3 0 5 5 7 8

Fig. 7. Experimental observation of cathodic convective diffusion boundary layer (Re = 500) by interruption technique. Cu deposition from 0.1M $CuSO_4$. Single crystal (111) face. Polycrystalline Cu with oxide film. Electrode 3.3 cm^2.

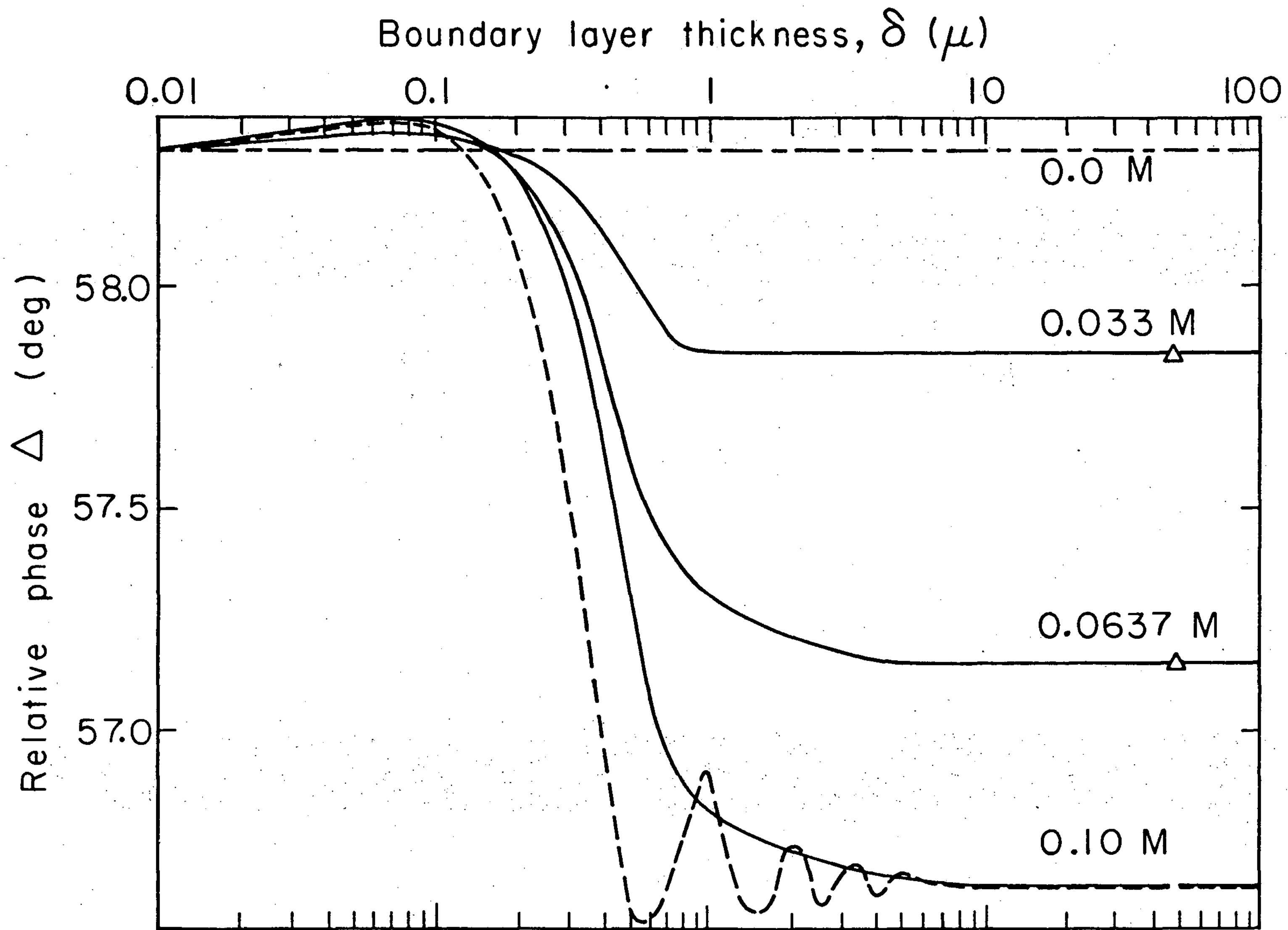
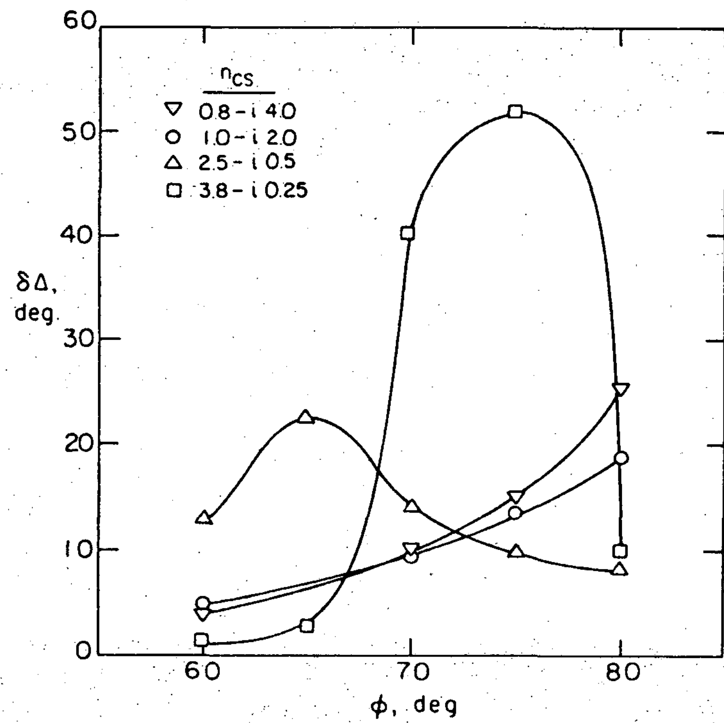


Fig. 1



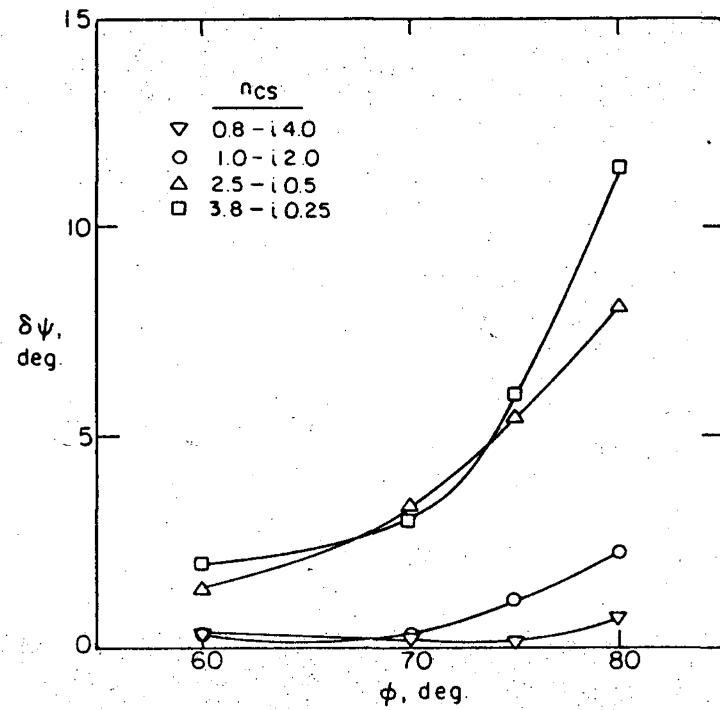
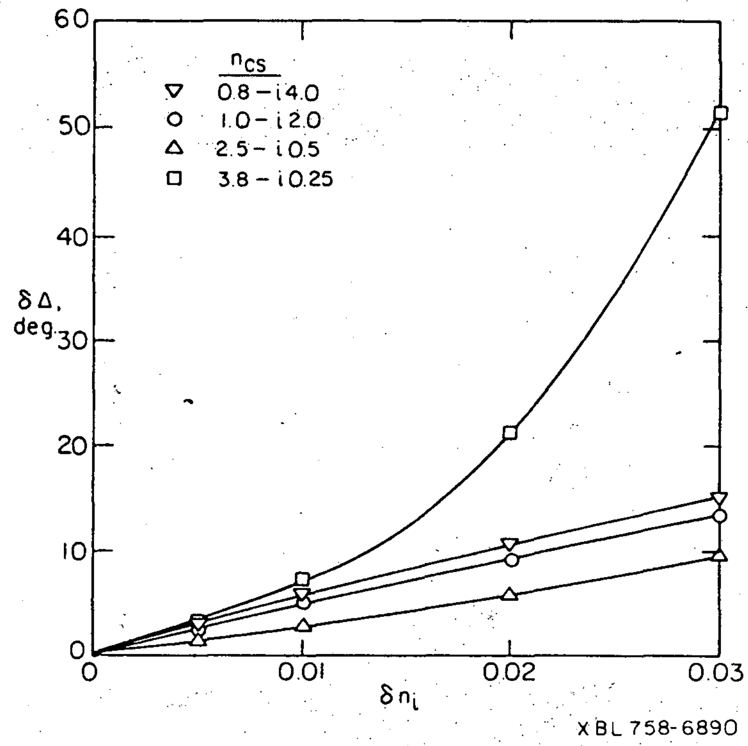


Fig. 2

0 0 0 0 4 3 0 5 5 7 9



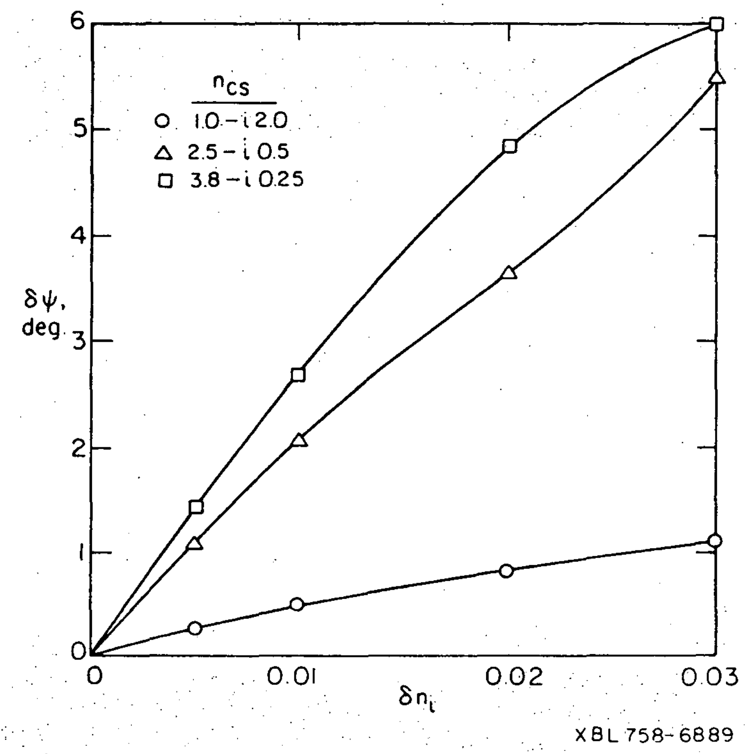


Fig. 3

0 0 0 0 4 3 0 5 5 8 0

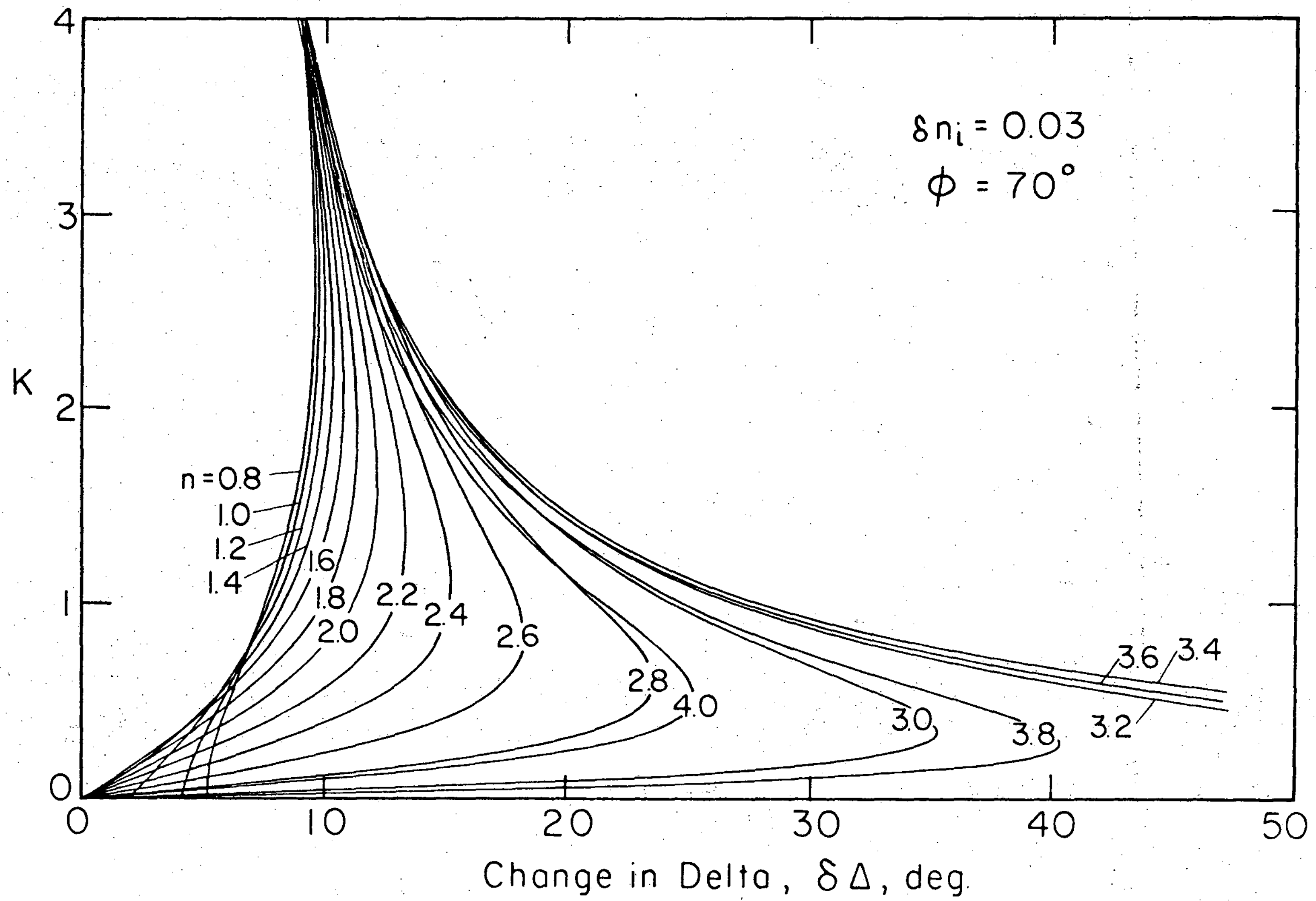


Fig. 4

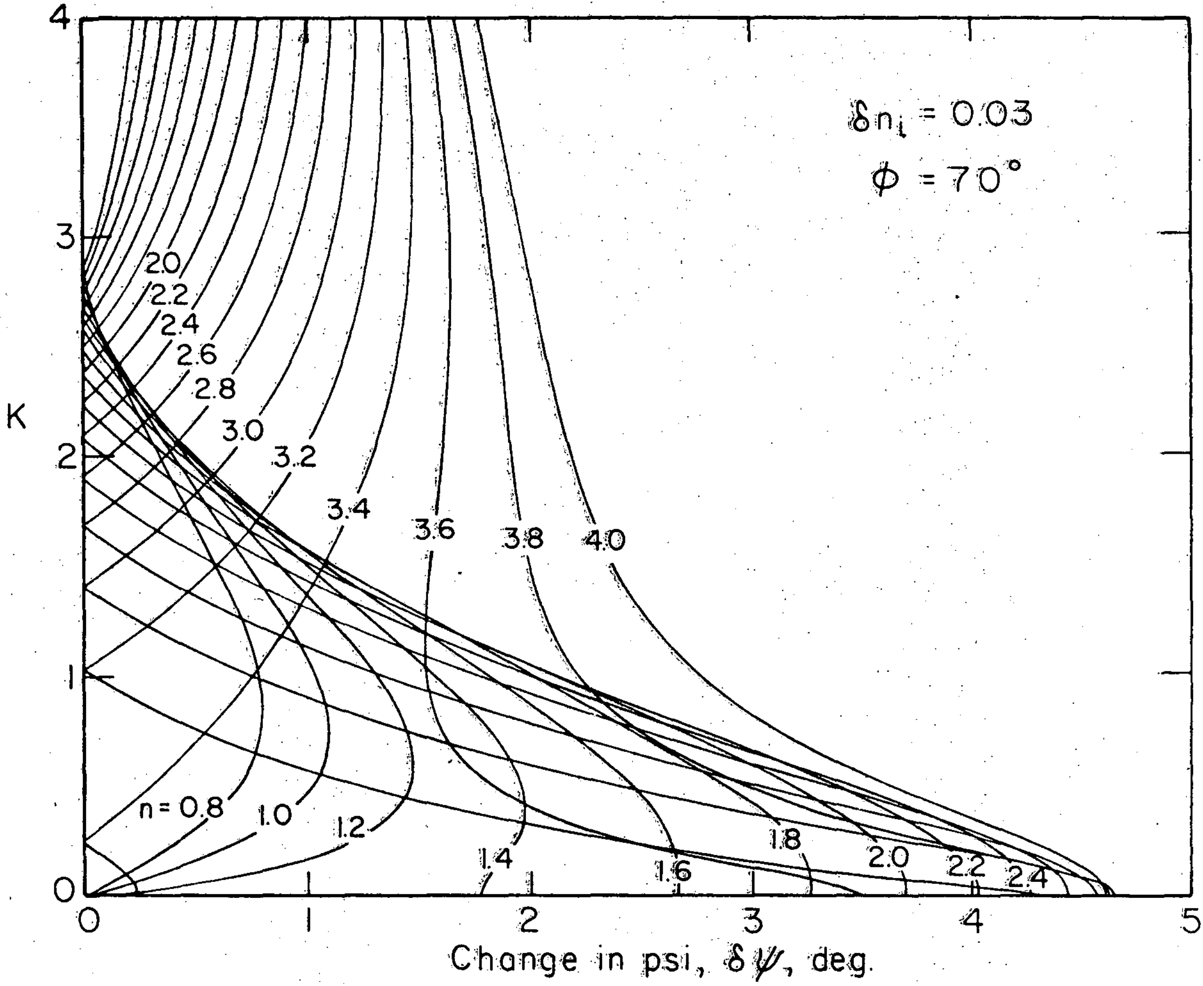
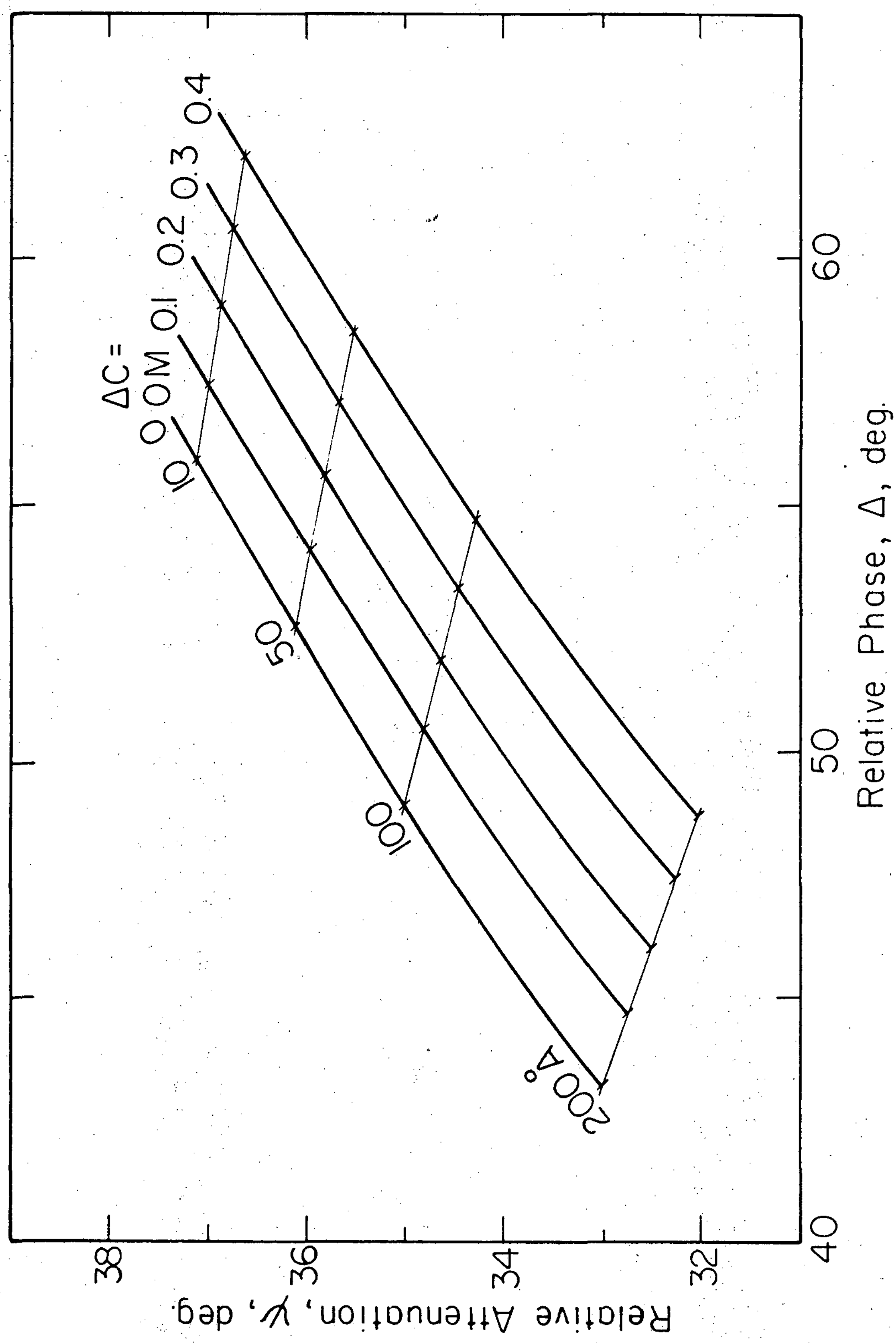


Fig. 5

0 0 0 0 4 3 0 5 5 8 1



XBL 758-6884

Fig. 6

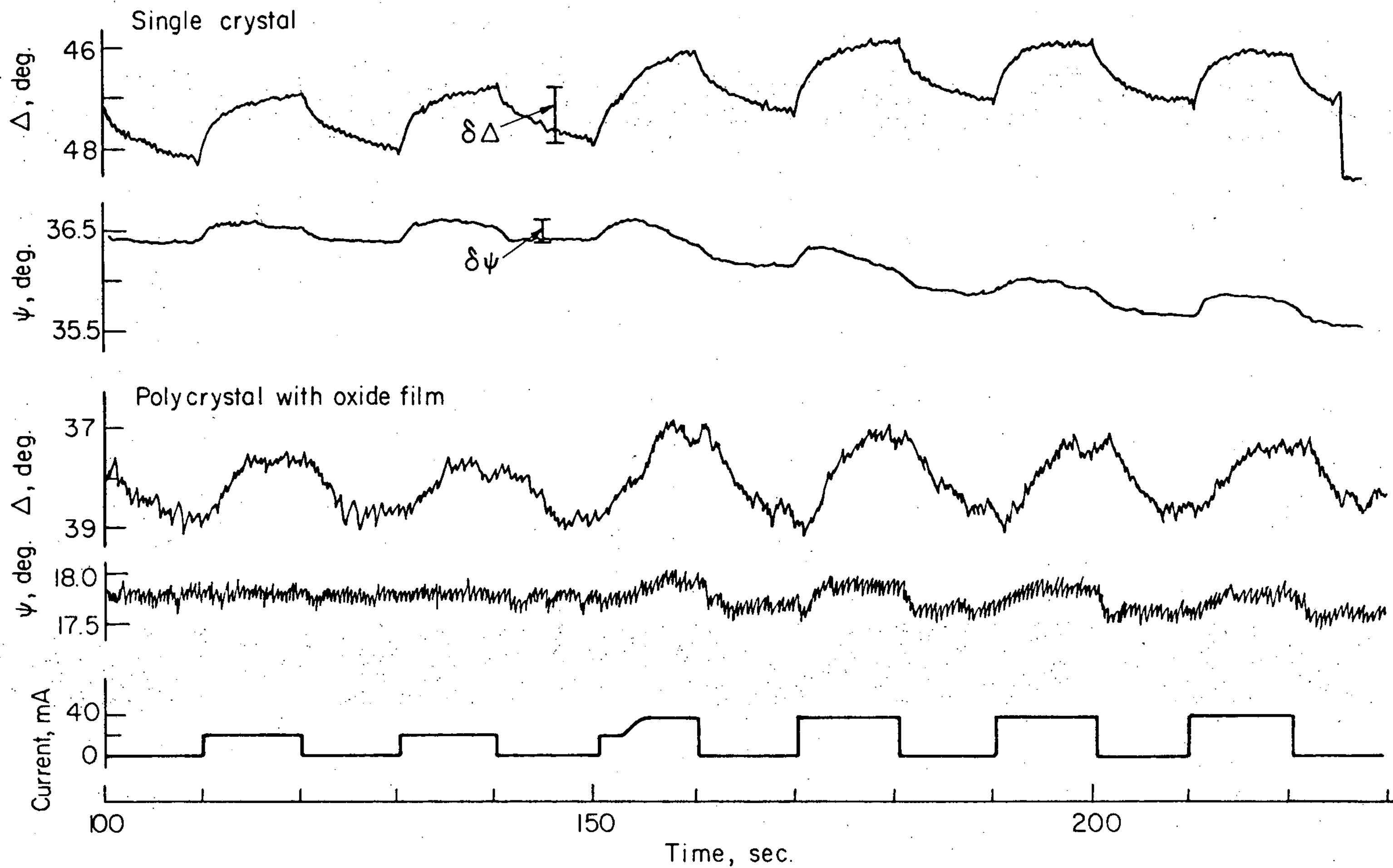


Fig. 7

0 0 0 0 4 3 0 5 5 8 2

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 Energy Research and Development Administration, 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