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MACROSCOPIC OPTICAL MODEL FOR THE ELLIPSOMETRY OF AN UNDERPOTENTIAL DEPOSIT: LEAD ON COPPER AND SILVER

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March 1983

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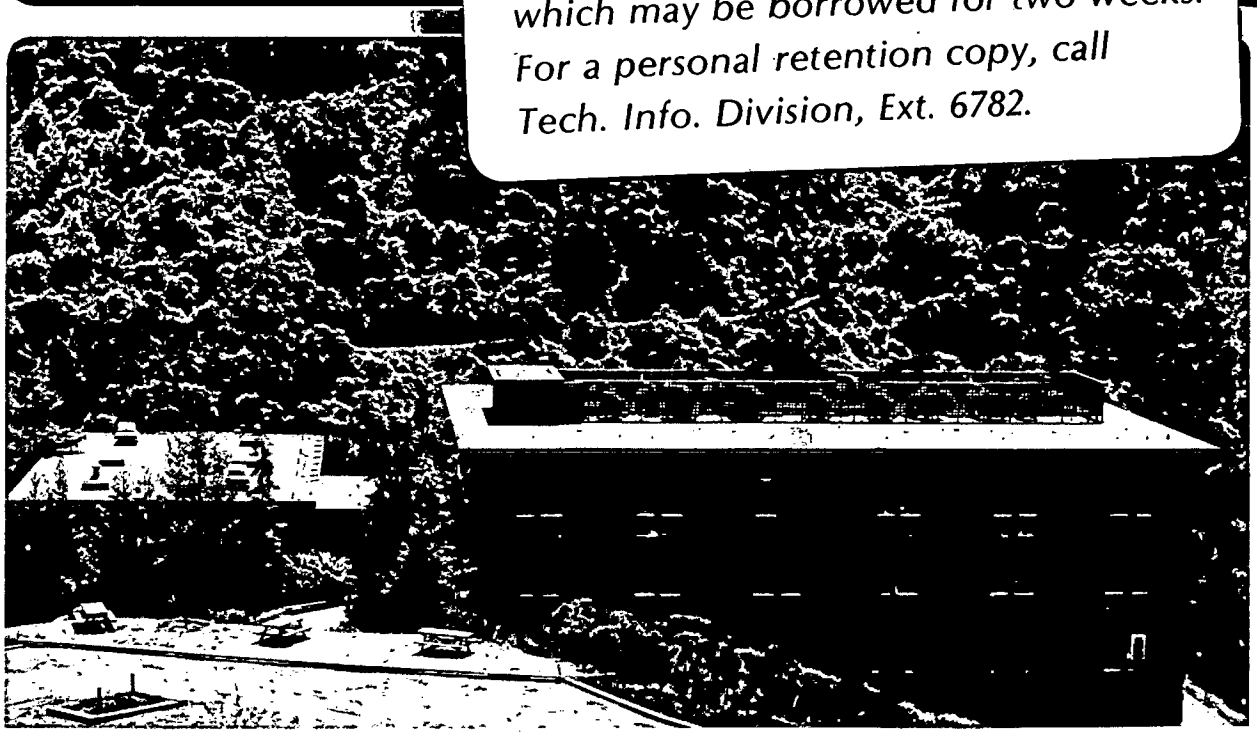

Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

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MACROSCOPIC OPTICAL MODEL FOR THE ELLIPSOMETRY OF AN UNDERPOTENTIAL DEPOSIT: LEAD ON COPPER AND SILVER

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ABSTRACT

Sub-monolayers of underpotential deposits of Pb on Ag and Cu substrates have been investigated in situ by ellipsometry during cyclic voltammetry. Predictions based upon several extrapolated macroscopic optical film models were compared to measurements. An island film model, in which film growth is assumed to occur by the spreading of monolayer film patches, provided good agreement with measurements. In this model the state of polarization of reflected light is determined by the coherent superposition of polarization states resulting from reflection on adjacent film-covered and bare surface elements. Fractional surface coverage and optical constants of the deposit, the independent variables in the model, were determined by multidimensional optimization over the entire range of coverage and confidence intervals for the parameters were determined by statistical analysis of the measurements.

Introduction

Formation of the first electrodeposited monolayer on a foreign substrate as an underpotential deposit presents a special opportunity for the study of metal monolayers because the deposition process can be controlled by the deposition potential and independently monitored by the measurement of electric charge. The nature of the underpotential deposit may be important for the properties of bulk deposits formed subsequently [1]. Nucleation and growth of underpotential deposits can be investigated *in situ* by simultaneous ellipsometry and cyclic voltammetry, however, optical models for sub-monolayers are needed to interpret the ellipsometer measurements.

The general theory of submonolayer ellipsometry has been reviewed by Bootsma, et al. [2,3]. These authors have discussed various approaches for modeling a layer of adatoms on a substrate, which included: (1) the Drude model; (2) Strachan's model; (3) Sivukin's model; and (4) an effective media film model based upon the Bruggeman theory. Other authors paid particular attention to the anisotropic nature of the adsorbate layer [4,5].

In the Drude model, the adsorbed layer is represented as a homogeneous, isotropic film of constant optical properties and increasing thickness. Fractional surface coverage is taken to be proportional to the increasing film thickness. This model employs three adjustable parameters, the complex refractive index and the thickness of the complete monolayer; it predicts a linear variation of the ellipsometer measurements delta and psi with surface coverage. The disadvantage of this model is that it is based on the unrealistic physical concept of representing a fractional monolayer as a film with a thickness less than one atomic diameter.

The Strachan model assumes a two-dimensional distribution of Hertzian oscillators, characterized by scattering indices for each of the three coordinate axes, at the interface. The oscillator strengths, and hence the scattering indices, increase with surface coverage. At low coverages, linear variations of delta and psi are predicted. This model has the advantage of being able to account for anisotropy normal to the interface and the disadvantage of requiring optical constants which cannot be interpreted in terms of established macroscopic properties (atomic dimensions and polarizabilities).

In the Sivukin model, the adsorbate layer is characterized by ratios of the interfacial polarizability to that of the substrate. This model also allows for anisotropy normal to the interface and has the advantage of using optical constants which can be interpreted in terms of macroscopic properties. However, calculations assume a nonabsorbing adsorbate layer. Knowledge of intermolecular distances between adjacent adatoms and between adatoms and substrate atoms is required; one must also know the adatom cross-section. The equations are very complicated and predict nonlinear variations in delta and psi with increasing fractional coverage.

Uniaxial anisotropy of the surface layer can also be accounted for with film models which are more macroscopic in nature. The adsorbate layer is given a thickness and extraordinary and ordinary complex refractive indices. This model has been used by the authors to explain results of spectroscopic ellipsometry for dyes adsorbed on various metallic surfaces (6). Unfortunately, such a model requires 5 adjustable parameters, four of which vary with surface coverage (the complex refractive indices);

adsorbate layer thickness has been assumed constant. Dependence of the optical constants on surface coverage is difficult to define. Such a model can be used when the extinction coefficient of the adsorbed layer shows a peak in the spectrum and exhibits dichroism, such as that caused by the preferred orientation of the electronic transition moment of a dye. The Pb underpotential deposit on Cu and Ag does not show these properties.

Experimental Procedure

Experiments were conducted potentiodynamically with measurements of the electrode surface being acquired with a fast, self-compensating instrument at a wavelength of 515 nm. The electrolyte was 5 mM $Pb(NO_3)_2$, 1 M $NaClO_4$ at pH 3. The single-crystal surfaces were approximately 1.2 cm x 2.85 cm and were mounted in epoxy. Electrodes were polished mechanically, ultimately using a water-base paste consisting of 0.05 micron alumina particles. The electrochemical cell was acrylic and held 250 ml of electrolyte. It had two quartz windows which allowed ellipsometry of the surface at a 75 degree angle-of-incidence. The potential of the working electrode was swept from 200 to -800 mV (vs. Ag/AgCl reference) at 1.5 V/min. Data acquisition and interpretation was done with a LSI-11 microcomputer. Details of the procedure and instrumentation are discussed elsewhere [1,6].

Effective Media Film Model

An effective media film model has been investigated in which the underpotential layer at submonolayer coverage is treated as a composite film of constant thickness consisting of randomly distributed Pb adatoms mixed with electrolyte (Fig. 1a). The volume fraction of Pb adatoms represents fractional coverage. The Bruggeman theory was used to compute

the apparent refractive index of this composite material. This model assumes that the underpotential layer is homogeneous and isotropic, and that its optical constants are independent of coverage. It requires only three adjustable parameters, optical constants of the monolayer and fractional coverage.

The most general form for mixing the dielectric properties of several materials is given in Eqn. 1 [7].

$$\frac{\hat{\varepsilon} - \hat{\varepsilon}_h}{\hat{\varepsilon} + 2\hat{\varepsilon}_h} = \sum_{i=1}^{n} \theta_i \frac{\hat{\varepsilon}_i - \hat{\varepsilon}_h}{\hat{\varepsilon}_i + 2\hat{\varepsilon}_h} \tag{1}$$

Each term in the summation represents a weighted contribution of the polarizabilities of individual components of the composite film which are related to the molecular polarizabilities through the Claussius-Mossotti equation (Eqn. 2).

$$\frac{\hat{\varepsilon}_i - 1}{\hat{\varepsilon}_i + 2} = \frac{4}{3} \pi N_i \alpha_i \tag{2}$$

For the binary composite of interest here, electrolyte and Pb adatoms, Eqn. 1 reduces to Eqn. 3.

$$\theta_{Pb} \frac{\hat{\varepsilon}_{Pb} - \hat{\varepsilon}_f}{\hat{\varepsilon}_{Pb} + 2\hat{\varepsilon}_f} + (1 - \theta_{Pb}) \frac{\hat{\varepsilon}_{soln} - \hat{\varepsilon}_f}{\hat{\varepsilon}_{soln} + 2\hat{\varepsilon}_f} = 0 \tag{3}$$

This simplification is important in that the complex dielectric constant of the composite film material (considered to be the host medium in Eqn. 1) can be determined by solving the resulting complex quadratic equation. The general multicomponent case requires finding n roots of an n-th degree complex polynomial, a formidable task. Equations 4 through 7 are used to compute the complex refractive index of the binary composite film; the

optical constants calculated from Eqn. 7 are substituted into the Drude equation and used to predict the ellipsometer parameters delta and psi.

$$\hat{A} = \frac{1}{2}\left[\hat{\varepsilon}_{Pb}(1 - 3\,\theta_{Pb}) + \hat{\varepsilon}_{soln}\,(3\,\theta_{Pb} - 2)\right] \tag{4}$$

$$\hat{B} = -\frac{1}{2}\left[\hat{\varepsilon}_{Pb}\,\hat{\varepsilon}_{soln}\right] \tag{5}$$

$$\hat{\varepsilon}_f = \frac{1}{2}\left[-\,\hat{A} \pm (\hat{A}^2 - 4\hat{B})^{1/2}\right] \tag{6}$$

$$\hat{n}_f = \hat{\varepsilon}_f^{\;1/2} \tag{7}$$

The root with the largest modulus is used to calculate the apparent optical constants (refractive index and extinction coefficient) of the composite layer (8). These equations are also applicable to binary porous films of thicknesses exceeding that of a monolayer (1). The experimentally determined values of delta and psi for different surface coverages of an underpotential deposit of Pb on Ag(111) are compared to predictions based upon the effective media film model in Fig. 2. The predictions are very nonlinear with increasing coverage, whereas the experimental measurements increase linearly. The optical constants and thickness of the monolayer used in this model were based on the measured values of delta and psi at complete coverage; optimization to minimize error for all levels of coverage was not performed. Clearly, this model is inadequate to describe the Pb underpotential deposit.

Island Film Model

A film model in which the underpotential deposit is formed as patches or islands of monolayer thickness has also been investigated. In this model, it is assumed that: (1) the optical constants of both the substrate and deposit are independent of potential and coverage; (2) the thickness of the island is the same as that of the complete monolayer; (3) the islands can be treated as equivalent homogeneous, isotropic layers; and (4) the islands are smaller than the lateral coherence of the incidence light. Implicit in these assumptions is that of negligible lateral interaction between neighboring islands as the deposit approaches a complete monolayer. Overall reflection coefficients for both s and p polarization states are calculated from weighted averages of those for the bare and film-covered areas (Eqn. 8).

$$r_\nu = \theta_f \cdot r_{\nu,f} + (1-\theta_f) \cdot r_{\nu,s} \tag{8}$$

These average reflection coefficients represent a coherent superposition of polarization states resulting from reflection on adjacent bare and film-covered surface elements. They are used to calculate the ratio of s and p Fresnel reflection coefficients (Eqn. 9).

$$\rho = \frac{r_p}{r_s} \tag{9}$$

This ratio is then substituted into the ellipsometry equation (Eqn. 10) for the calculation of the ellipsometer parameters delta and psi.

$$\rho = \tan(\psi) \exp(-i\Delta) \tag{10}$$

This model also has only three adjustable parameters, the thickness and optical constants of the underpotential deposit. Predictions by the island film model using the same optical constants and thickness as used for the effective media model, (Fig. 2) are presented in Fig. 3; also without optimization over the entire range of coverage. Qualitatively, this model predicts linear variations of delta and psi with coverage, as observed experimentally.

Optimization and Confidence Intervals for the Parameters of the Island Film Model

The island film model has been optimized for the Pb underpotential deposit formation on both Ag(111) and Cu(111), by minimizing the sum-of-squares error between measurements and predictions over the entire range of coverage (Eqn. 11).

$$S_{\Delta,\psi} = \sum_{i=1}^{N} (\Delta_{M,i} - \Delta_{C,i})^2 + \sum_{i=1}^{N} (\Psi_{M,i} - \Psi_{C,i})^2 \tag{11}$$

The optimized values of the model parameters are given in Table I and model predictions of delta and psi resulting from the use of these parameters are compared to experimental measurements for Ag(111) and Cu(111) substrates in Figs. 4 and 5. Agreement is very good.

Table I also gives confidence intervals of the model parameters. These intervals were calculated from parameter variances, as shown in Eqn. 13.

$$SE(p) = \frac{\sigma^2}{\frac{1}{2}\frac{\partial^2 S_{\Delta,\psi}}{\partial p^2}} \tag{12}$$

$$\delta(p) = t(2N - P, 1 - 2\alpha)[SE(p)]^{1/2} \tag{13}$$

Computation of the confidence interval involves the Student-t statistic for "2N-P" degrees-of-freedom and a specified level of confidence, where "N" is the number of ellipsometer measurements and "P" is the number of adjustable model parameters; in this case there were 17 degrees-of-freedom and a 95% level of confidence level was specified. The parameter variances were estimated numerically (Eqn. 14) and required that the model variance also be estimated numerically (Eqn. 15).

$$\sigma^2 \sim S_{MIN}/df = S_{MIN}/(2N - P) \tag{14}$$

$$\frac{1}{2}\frac{\partial^2 S_{\Delta,\psi}}{\partial p^2} \sim \frac{S_{(+)} + S_{(-)} - 2\, S_{MIN}}{2(\Delta p)^2} \tag{15}$$

The parameter variances are indicative of the curvature in the sum-of-squares hypersurface due to the respective parameters, and can be used to determine the relative sensitivity of the model to errors in parameter values [9].

The complex refractive index of the substrates used in these calculations was determined experimentally by ellipsometry of the bare surface before formation of the underpotential deposit. Results agree with literature values. The refractive index of the incident medium was obtained from the literature.

Conclusions

1. As the Pb underpotential deposit layer forms on Ag(111) and Cu(111) the ellipsometer parameters delta and psi vary linearly with coverage.
2. The effective media film model, based upon the gradual filling of a monolayer by randomly distributed adatoms, with optical constants of an equivalent film determined by use of the Bruggeman theory, does not agree with experimental measurements and predicts very nonlinear variations of delta and psi with coverage.
3. A new extrapolated macroscopic model, based upon the lateral growth of a patchwise distributed island film, with the polarization of the reflected light determined by the coherent superposition of polarization states, explains the experimental data well and contains the fractional surface coverage explicitly.
4. Optimization of the three adjustable parameters of the island film model over the entire range of coverages allows one to calculate confidence intervals for the parameters determined.
5. The thicknesses of the Pb underpotential deposits on Cu(111) and Ag(111) were determined to be about 3.5 and 4.1 Angstroms, respectively. These values are comparable to the atomic diameter of Pb. The complex refractive indices of the surface layers on Cu(111) and Ag(111) were approximately 1.23 - 3.52i and 1.29 - 4.08i, respectively.

Acknowledgments

We wish to thank Professor W. Plieth for use of the light scattering cell. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under contract no. DE-AC03-76SF00098.

Table I. Optical properties of the Pb underpotential deposit (UPD) at complete coverage (θ=1).

Wavelength of light, 5145Å; temperature, 25°C; electrolyte, 0.5 and 5.0 mM Pb^{++} 1M $NaClO_4$; pH 3.

Errors given for 95% level of confidence and based upon 37 degrees of freedom, assuming applicability of the coherent superposition model. Errors introduced by uncertainty in n_a and n_s, (determined experimentally) not taken into account.

Substrates		Ag(111)	Cu(111)	Cu(111)
Pb concentration in electrolyte		0.5 mM	0.5 mM	5 mM
Ambient refractive index	n_a	1.340	1.340	1.340
UPD refractive index	n_{UPD}	1.285±0.007	1.225±0.066	0.952±0.417
UPD extinction coeff.	k_{UPD}	4.080±0.040	3.520±0.041	3.898±0.021
UPD thickness	d_{UPD}	5.149±0.026	4.030±0.178	4.777±1.101
Substrate refractive index	n_s	0.174	0.788	0.853
Substrate extinction coeff.	k_s	3.215	2.408	2.347

NOMENCLATURE

df	degrees of freedom, 2N-P
$\hat{n}_f$	complex refractive index of film
p	the number of model parameters to be fitted
r_ν	Fresnel reflection coefficient for polarization ν (s or p)
$r_{\nu,f}$	Fresnel reflection coefficient for film covered surface
$r_{\nu,s}$	Fresnel reflection coefficient for bare surface
$t(2N-P, 1-2\alpha)$	the t-statistic for "2N-P" degrees-of-freedom at a "$1-2\alpha$" level of confidence
$\hat{A}$, $\hat{B}$	complex parameters for quadratic equation
N	the number of pairs of Δ and ψ measurements
N_i	atomic number density of component i in the effective medium
P	the number of model parameters to be fitted
SE(p)	the variance of parameter p
$S_{\Delta,\psi}$	sum-of-squares error between theoretical ellipsometer parameters and those measured experimentally
S_{MIN}	the minimum value of $S_{\Delta,\psi}$ corresponding to a selection of optimum p values
$S_{(+)}$	a value of $S_{\Delta,\psi}$ computed at a parameter value of $p + \Delta p$
$S_{(-)}$	a value of $S_{\Delta,\psi}$ computed at a parameter value of $p - \Delta p$

α	level of confidence, $1-2\alpha$
α_i	molecular polarizability of component i in the effective medium
$\delta(p)$	the error in parameter "p" at a "$1-2\alpha$" level of confidence
$\hat{\varepsilon}$	complex dielectric constant of the effective medium
$\hat{\varepsilon}_f$	effective complex dielectric constant of thin-film deposit
$\hat{\varepsilon}_h$	complex dielectric constant of the host medium
$\hat{\varepsilon}_i$	complex dielectric constant of component i making up the effective medium
$\hat{\varepsilon}_{Pb}$	complex dielectric constant of Pb
$\hat{\varepsilon}_{soln}$	complex dielectric constant of electrolyte
ρ	ratio of complex reflection coefficients
σ^2	the variance of the model predictions for Δ and ψ
θ_f	fraction of surface covered by film of refractive index $\hat{n}_f$
θ_i	volume fraction of component i in the effective medium
θ_{Pb}	volume fraction of Pb in composite thin-film deposit
Δ	ellipsometer parameter, phase difference between p and s electric field components after reflection, relative to the incident (degrees)
$\Delta_{c,i}$	calculated value of Δ
$\Delta_{M,i}$	measured value of Δ

ψ	ellipsometer parameter, amplitude ratio of p and s electric field components after reflection ($\tan \psi$), relative to the incident (degrees)
$\psi_{c,i}$	calculated value of ψ
$\psi_{M,i}$	measured value of ψ

Figure Captions

1. Schematic representation of the macroscopic equivalent film models tested for the Pb underpotential deposit on Ag and Cu(111). (a.) Increasing refractive index of film with constant (atomic dimension) thickness (effective media model). (b.) Increasing coverage by spreading film patches of constant thickness and refractive index (Island model).
2. Comparison of the changes in ellipsometer response as a function of coverage θ predicted by the effective media model to the experimental data for underpotential deposit formation on Ag(111). Wavelength 515 nm, angle of incidence 75°. Optical properties of the underpotential deposit derived from ellipsometer measurements at full coverage. Surface coverage determined by measurement of charge passed during deposit formation.
3. Comparison of the changes in ellipsometer response predicted by the island model before optimization of parameters to the experimental data for the Ag(111) substrate. Wavelength 515 nm, angle of incidence 75°.
4. Optimized island model (line) for the Pb underpotential deposit on Ag(111) and measured points.
5. Optimized island model (line) for the Pb underpotential deposit on Cu(111) and measured points.

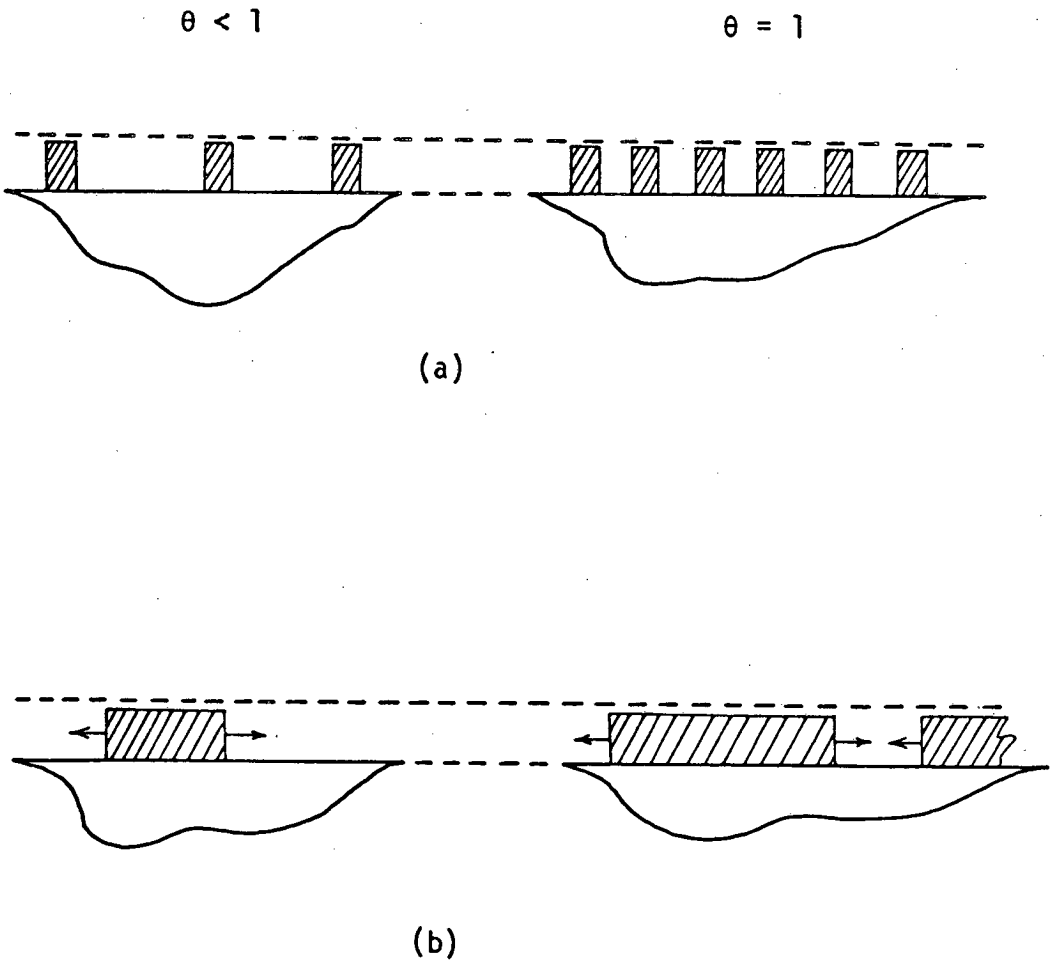

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Fig. 1

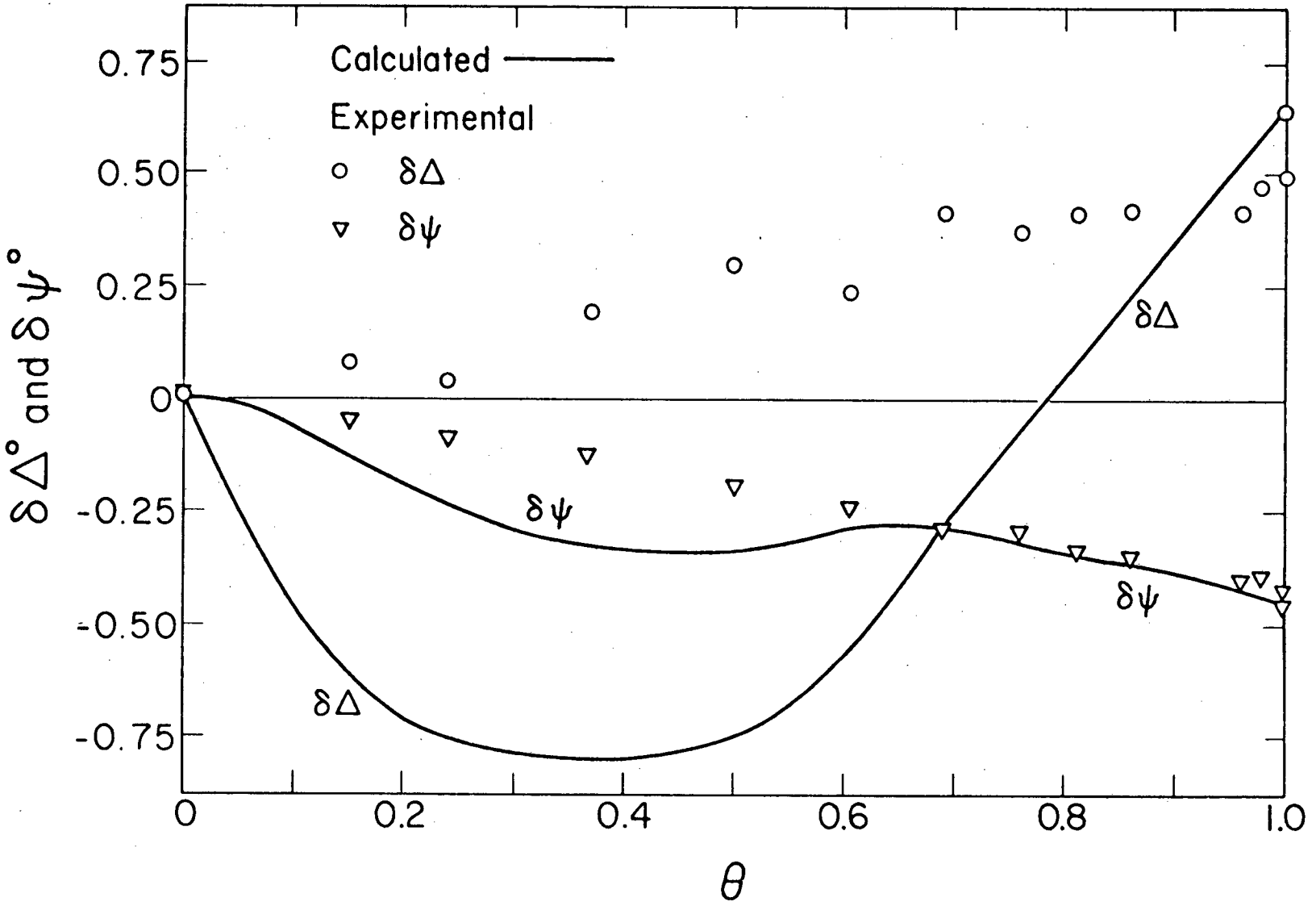

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Fig. 2

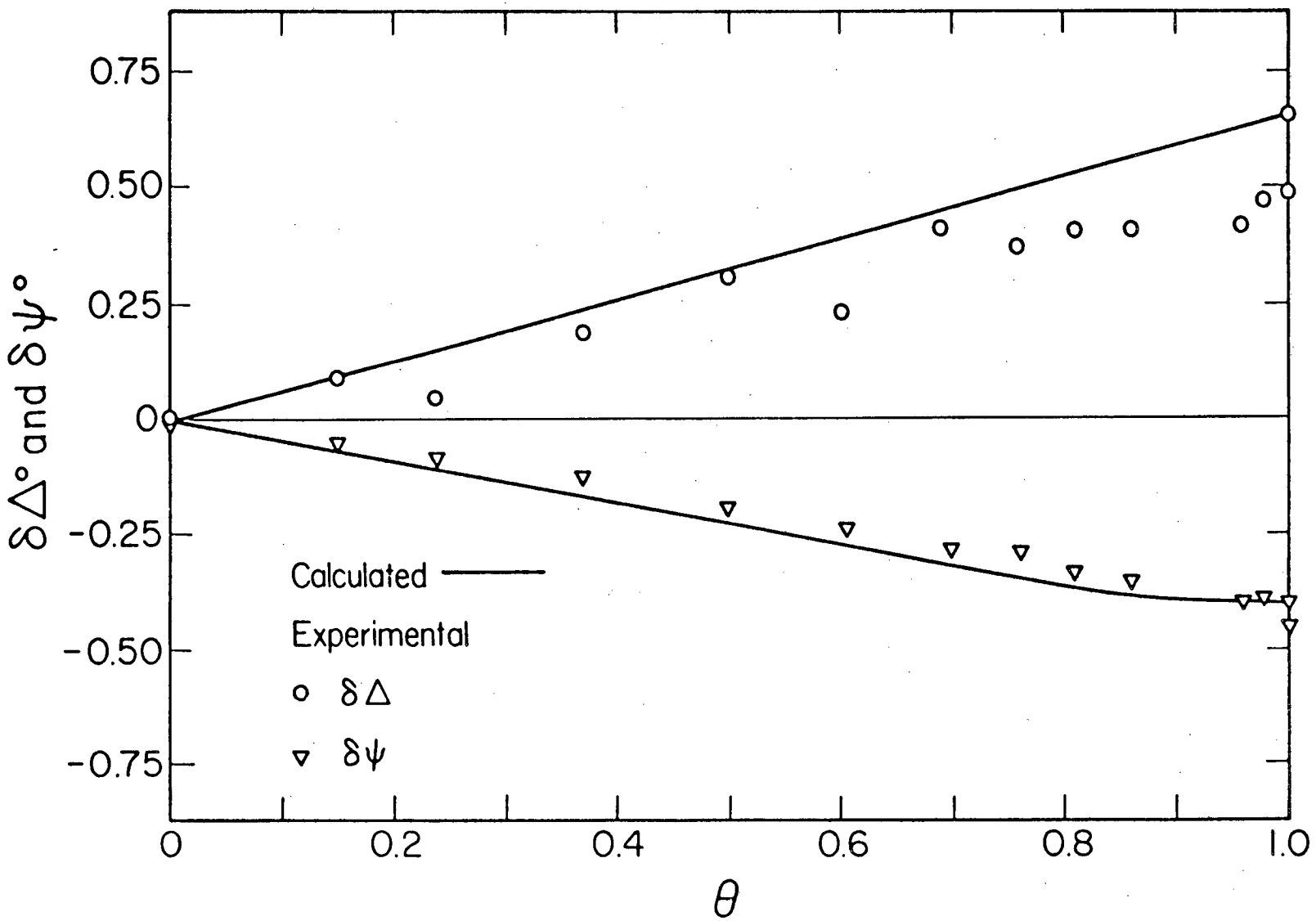

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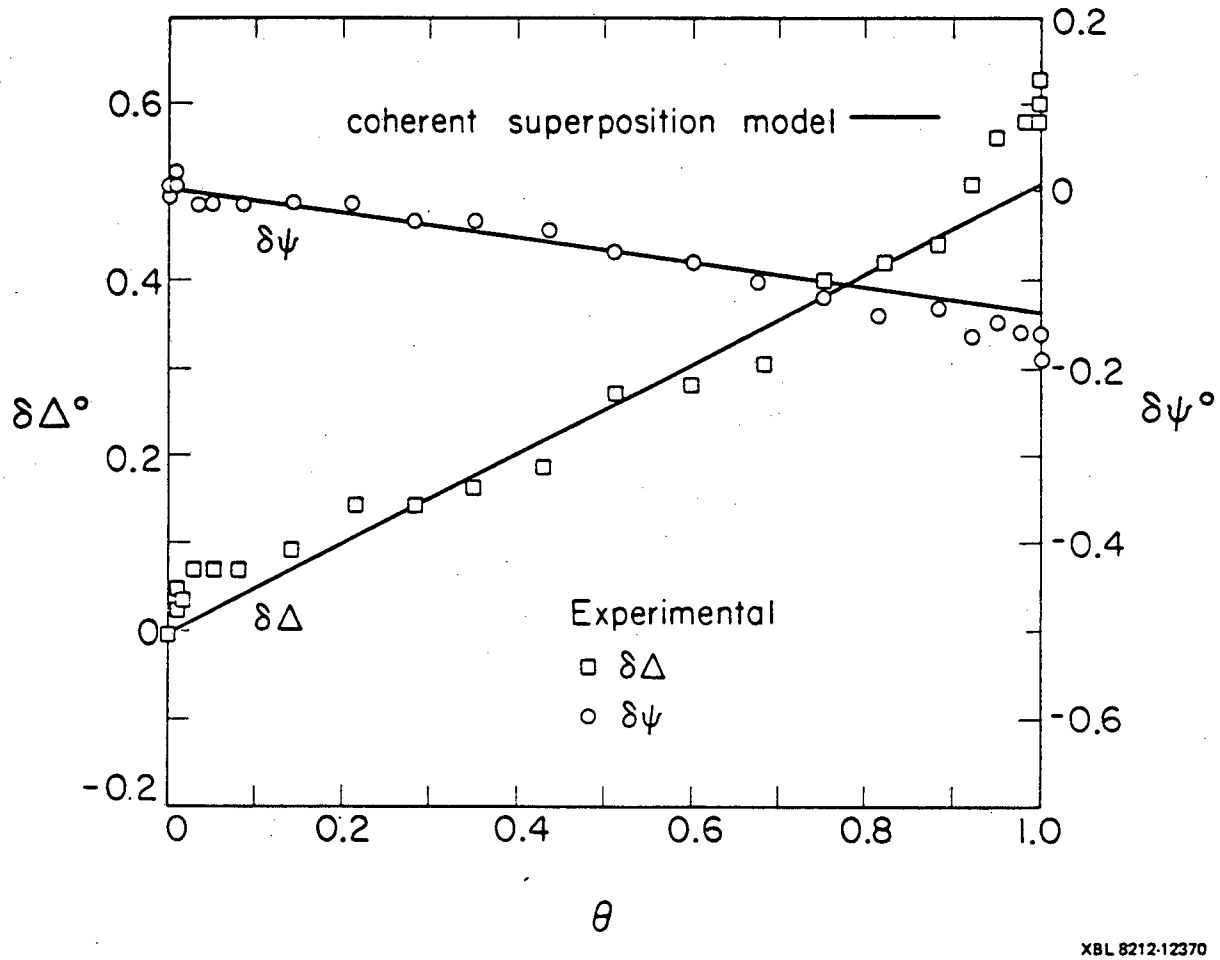
Fig. 3


coherent superposition model
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δΔ
Experimental
δΔ
δψ
δΔ°
δψ°
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0.2
0
-0.2
0.2
0
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Fig. 4

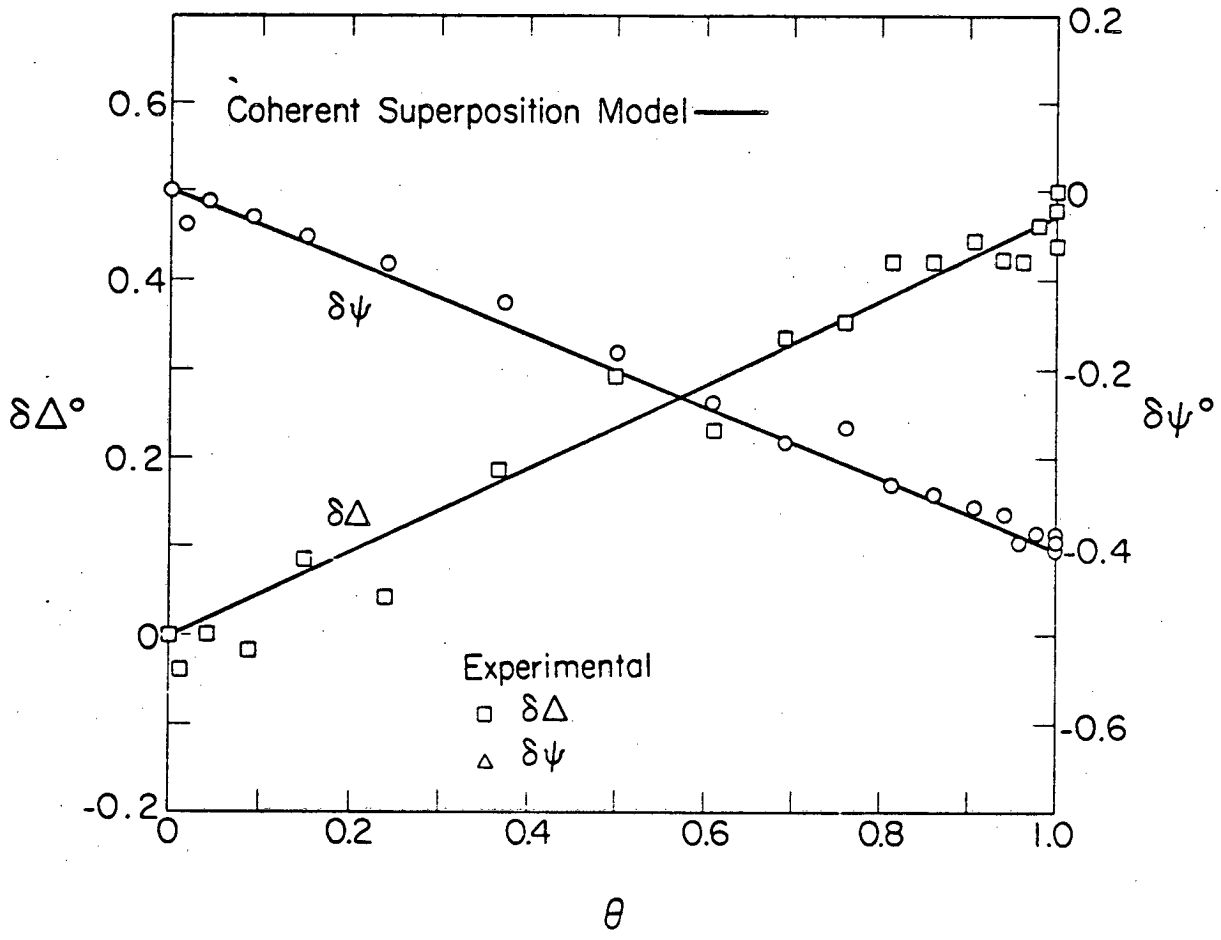

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Fig. 5

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