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TWO-DIMENSIONAL COMPRESSIBILITY OF ELECTROCHEMICALLY ADSORBED LEAD ON SILVER (III)

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### Author

Melroy, O.R.

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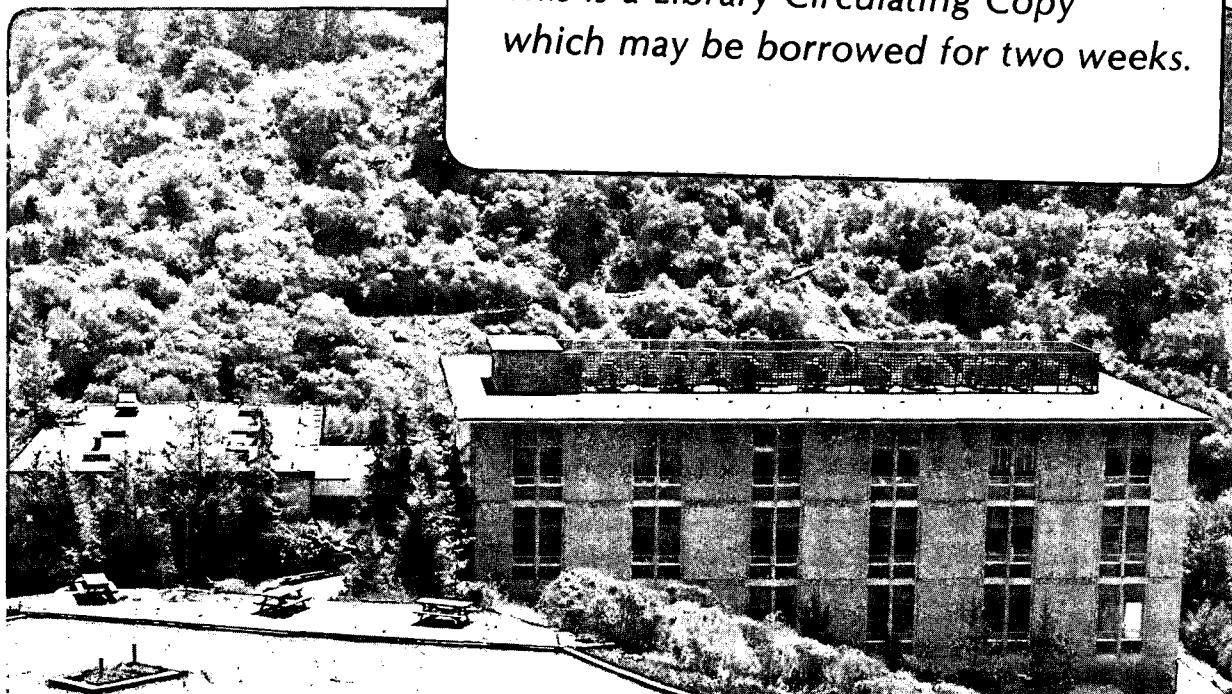
### Two-dimensional Compressibility of Electrochemically Adsorbed Lead on Silver (III)

O.R. Melroy, M.F. Toney, G.L. Borges,  
M.G. Samant, J.B. Kortright,  
P.N. Ross, and L. Blum

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TWO DIMENSIONAL COMPRESSIBILITY OF ELECTROCHEMICALLY  
ADSORBED LEAD ON SILVER (111)

O.R. Melroy, M.F. Toney, G.L. Borges, and M.G. Samant

IBM Alamden Research Center  
650 Harry Road  
San Jose, CA 95120

J.B. Kortright and P.N. Ross

Lawrence Berkeley Laboratory  
University of California  
Berkeley, CA 94720

L. Blum

Physics Department  
College of Natural Sciences  
P.O. Box AT  
Rio Piedras, Puerto Rico 99831

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Rio Piedras, Puerto Rico 99831

**Abstract**

We report the two dimensional compressibility of electrochemically deposited lead on silver (111). Measurements were made in-situ (in contact with solution) using grazing incidence x-ray scattering. Between monolayer formation and bulk deposition, the near-neighbor distance of the lead monolayer decreased linearly with applied potential (proportional to the chemical potential). Since the lead monolayer is in equilibrium with lead ions in solution, the isothermal compressibility of the monolayer can be calculated from the potential dependence of the near-neighbor distance and is  $0.98 \text{ \AA}^2/\text{eV}$ . Implications of the high strain in the monolayer on the wetting behavior of lead are discussed.

Adsorbed monolayers are of fundamental interest, since they provide physical realizations of two dimensional (2D) condensed matter. Considerable effort has been devoted to studying monolayers of gases physically adsorbed from the vapor phase onto graphite and metal substrates.<sup>1-10</sup> The isothermal compressibility ( $\kappa_2$ ) of rare gas monolayers has been measured and agrees well with that calculated theoretically using relatively simple molecular interactions.<sup>3-6</sup> However, the compressibility of metallic adlayers has received far less attention due to inherent difficulties in making equilibrium adsorption measurements. Realistic calculations of  $\kappa_2$  for metals are also considerably more difficult, since two dimensional band structure calculations that include the effect of the substrate are necessary. In this paper, we report in in-situ grazing incidence x-ray scattering (GIXS) investigation of electrochemically adsorbed lead on silver (111). Both the room temperature compressibility of the monolayer with applied potential and the wetting behavior have been studied.

Electrochemical deposition of metals onto a foreign metal substrate frequently occurs in distinct stages.<sup>11</sup> The initial steps, corresponding to the formation of different ad-layers on the electrode surface, occur at electrode potentials positive (i.e., anodic) of the reversible thermodynamic potential for bulk deposition and hence are termed underpotential deposition (UPD). On single crystals, the different peaks in the current/potential profile prior to bulk deposition correspond to the formation of well defined, presumably ordered, ad-layers.<sup>12-16</sup> The current response to a linear sweep of potential for lead on silver (111) is shown in Fig. 1, together with the charge integral of this sweep.

Under ideal conditions, the latter can also be regarded as an adsorption isotherm.<sup>11</sup> The first peak at approximately -350 mV corresponds to the deposition of a single monolayer of lead. That this layer is an incommensurate, close-packed hexagonal monolayer had been inferred using a variety of techniques<sup>12-14,17</sup> and was recently confirmed in an in-situ GIXS experiment.<sup>18</sup> Between the peak in the current at -350 mV and the onset of bulk deposition (-550 mV), a single monolayer of lead, in equilibrium with the lead ions in solution, is adsorbed on the silver surface. Varying the potential in this region between monolayer formation and bulk deposition changes the chemical potential of the Pb atoms in the 2b layer and is thus analogous to varying the vapor pressure of a gas in equilibrium with its physisorbed monolayer.

The presence of the condensed phase (electrolyte) over the electrode, of course, greatly complicates measurements of UPD monolayers. Most techniques that give direct surface structural information are based on scattering of ions or electrons and are unsuitable of use outside high vacuum. Ex-situ surface science techniques such as LEED and RHEED have been used to study the structure of layers adsorbed from solution and have provided valuable information.<sup>15</sup> However, these methods require transfer of the sample from the electrochemical environment, which introduces questions about surface rearrangement upon removal of the electrolyte and loss of potential control. GIXS is, however, ideally suited for in-situ structural measurements of solid-liquid interface.

GIXS is a well established technique and has been applied to the structural determination of surface reconstruction on metals<sup>19</sup> and sem-

iconductors,<sup>20</sup> to melting of adsorbed monolayers,<sup>21</sup> and the characterization of solid/solid interfaces.<sup>22</sup> To use GIXS to study UPD monolayers, a suitable electrochemical cell was developed that allows deposition with a relatively thick layer of electrolyte covering the electrode.<sup>18</sup> The cell is then reconfigured such that a very thin electrolyte layer covers the electrode. The thinness of this layer greatly reduces scattering from the electrolyte.

The electrode preparation and electrochemical cell have previously been described in detail and will not be discussed here.<sup>18</sup> Lead was electrochemically deposited at room temperature on the silver (111) electrode at -400 mV (vs. Ag/AgCl) from a 0.1 M sodium acetate, 0.1 M acetic acid and  $5 \times 10^{-3}$  M lead acetate solution. The cell was then changed into the thin layer configuration and experiments at different potentials conducted by varying the potential after the reconfiguration. The x-ray diffraction data were collected at the Stanford Synchrotron Radiation Laboratory (SSRL) under dedicated beam conditions on a focussed 54-pole wiggler beam line (VI-2) equipped with a Huber four circle diffractometer on which the electrochemical cell was mounted. The sample was held in the vertical plane and the scattered radiation collected at an exit angle equal to the (grazing) incidence angle. The incident x-ray beam energy was chosen to be 12350 eV (1.003 Å) using a silicon (220) double crystal monochromator and calibrated with the diffraction from a silicon (111) crystal.

At potentials where lead is adsorbed (negative of -375 mV), diffraction from the lead monolayer was observed. Radial and azimuthal scans of the (10) reflection of the lead monolayer with the electrode



held at -550 mV were shown in Fig. 2. The diffuse background scattering is largely due to the thin layer of solution covering the electrode. The peak in the radial scan appears at  $Q = 2.13 \text{ \AA}^{-1}$  corresponding to a lead-lead near neighbor distance of  $3.40 \text{ \AA}$  for the incommensurate close packed monolayer. The lead monolayer is not aligned along a silver symmetry direction, but is rotated  $4.5^\circ$  from the silver  $(\bar{2}11)$  direction.

As the potential of the electrode decreased from -375 to -550 mV, the scattering vector of the lead reflection increased. A plot of the lead-lead near neighbor distance vs. electrode potential is shown in Fig. 3. The near neighbor distance decreased linearly with potential until the onset of bulk deposition. At this potential, the near neighbor distance is  $3.40 \text{ \AA}$ , a 2.8% contraction from bulk lead. No additional change in the spacing was observed for potentials set cathodic to the potential for the onset of bulk lead deposition, where multilayer growth is thermodynamically favored.

The two dimensional (2D) isothermal compressibility  $\kappa_2$  is defined as:<sup>2</sup>

$$\kappa_2 = -\left(\frac{1}{a}\right) \left(\frac{\partial a}{\partial \phi}\right)_T = -\left(\frac{\partial a}{\partial \mu}\right)_T \quad (1)$$

where  $\phi$  is the 2D spreading pressure,  $a$  is the atomic area, and  $\mu$  is the chemical potential. For a physisorbed monolayer in equilibrium with its (ideal gas) vapor,<sup>2</sup>  $d\mu = -k_B T(d \ln P)_T$ . This equilibrium relationship has been used in previous experimental measurements of  $\kappa_2$  (Refs. 3-6) of gas monolayers. Similar experiments on metallic ad-layers have not been possible because the very low vapor pressure of the metals necessitates the use of nonequilibrium conditions. However, changing the applied

potential in electrochemical adsorption experiments is analogous to changing the vapor pressure in vapor/solid experiments, since the chemical potential is related to the applied potential (V) as:<sup>23</sup>

$$d\mu = -z e dV \quad (2)$$

where  $z$  is the number of electrons transferred per atom deposited at  $e$  is the electron charge. Thus  $\kappa_2$  can be determined from equilibrium measurements of either pressure or applied potential. However, in electrochemical experiments the potential can be accurately controlled over a wide range without the experimental difficulties of controlling and measuring pressure over a large range ( $d\mu = d \ln P$ ).

For a close-packed triangular layer,  $a = \frac{\sqrt{3}}{2} r^2$ , and

$$\kappa_2 = \frac{\sqrt{3}r}{ze} \left( \frac{\partial r}{\partial V} \right)_T \quad (3)$$

Evaluating the slope from Fig. 3 and substituting above, the value obtained for  $\kappa_2$  is  $0.98 \text{ \AA}^2/\text{eV}$ . This is in reasonable agreement with that ( $1.2 \text{ \AA}^2/\text{eV}$ ) estimated for a 2D Sommerfeld model (non-interacting free electron gas),<sup>24</sup> which is probably a result of the free-electron nature of lead. A more realistic calculation would involve a 2D band structure calculation that included effects of the silver substrate and is outside the scope of this letter. Since the slope in Fig. 3 is constant,  $\kappa_2$  is independent of near-neighbor spacing, to within 3%. This is unexpected, since in bulk lead the compressibility drops by 7% when the near neighbor distance decreases from 3.45 to 3.40 \AA.<sup>25</sup>

As shown in Fig. 2, the angle between the lead (10) reflection and the silver ( $\bar{2}11$ ) direction (rotational epitaxy angle) is  $4.5^\circ$ . No

change in this angle was observed with the compression of the ad-layer.

This was an unexpected observation since the application of the models developed either by Novaco and McTague<sup>7</sup> (weakly modulated overlayer) or Shiba<sup>8</sup> (large modulations in adatom-substrate energy) predict  $0.5^\circ$  or more changes in the rotation epitaxy angle for ca. 3% compression. Also, we were unable to detect any satellite diffraction that would result from a strong periodic modulation in the ad-layer as would be expected from an incommensurate overlayer structure. However, the presence of diffuse scattering from the electrolyte prevents the observation of a satellite with less than 3% of the intensity of the (10) peak.

As shown above, at the potential for bulk deposition, the ad-layer is highly strained. Recent theories on wetting<sup>26-28</sup> have suggested that, in addition to the ratio between substrate-adsorbate and adsorbate-adsorbate interaction, strain in the adsorbed layers is an important factor in determining wetting behavior. This strain is compression resulting from a strong adsorbate-substrate interaction. Although these theories were developed for physisorption and the detailed calculations are not applicable in our case, the idea that strain is a dominant factor in wetting behavior is relevant. At potentials where bulk lead was deposited, no change in the intensity of the adsorbate diffraction was observed. Apparently the second layer of lead that forms is not in registry with the first. In addition, no new diffraction spots were observed from bulk lead, indicating that bulk lead is initially deposited as randomly oriented three dimensional islands (incomplete wetting). Although the observation of incomplete wetting is expected from the strain factor in wetting theory, care must be taken in

drawing exact analogies between vacuum and electrochemical deposition. Solvent and electrolyte adsorption occurring concurrently with metal deposition are also important factors in determining the structure of electrochemically deposited layers. Electrochemical deposition, however, has the advantage of allowing equilibrium measurements. Just as this allows the two dimensional compressibility of metals to be measured, studies of electrochemical deposition in ideally selected metal/electrolyte systems may also lead to significant insight into wetting behavior.

In summary, the variation in the lead near neighbor distance with applied potential was measured and the 2D isothermal compressibility determined for electrochemically adsorbed lead monolayers on silver (111). This equilibrium measurement is possible for metals because the chemical potential can easily be varied and the in-plane near neighbor distance measured in-situ using GIXS. In-situ structural studies of the solid-liquid interface are now possible using techniques such as GIXS and will lead to a greater understanding of nucleation at this interface. The ability to make equilibrium measurements at this interface should also enhance our understanding of 2D layers.

#### Acknowledgements

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**Figure Captions**

- Figure 1. Current-voltage and charge-voltage curves for the deposition of lead on silver (111). 10 mV per sec. Potential is relative to a Ag/AgCl reference electrode.
- Figure 2. The (10) reflection of the lead monolayer on silver (111) at -550 mV. The silver ( $\bar{2}11$ ) is defined as  $\phi = 0$ . a) Rocking scan at  $Q = 2.13 \text{ \AA}^{-1}$ . b) Radial scan at  $\phi = 4.5^\circ$ . The  $0.02 \text{ \AA}^{-1}$  width of the peak indicates a domain size of about  $290 \text{ \AA}$ .
- Figure 3. Lead-lead near neighbor distance vs electrode potential. The UPD monolayer adsorbs at -375 mV and bulk lead is deposited at -550 mV.



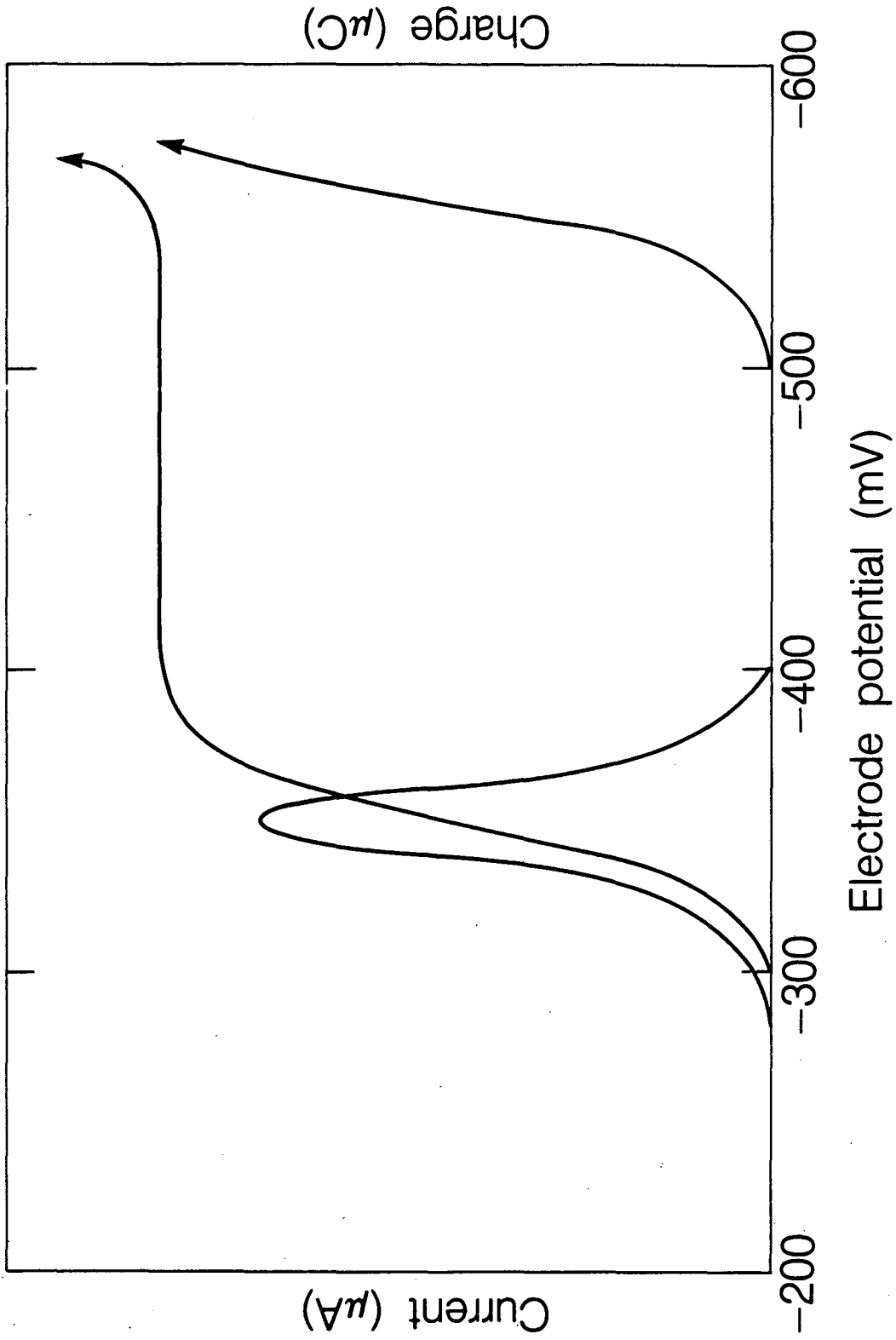


Fig. 1

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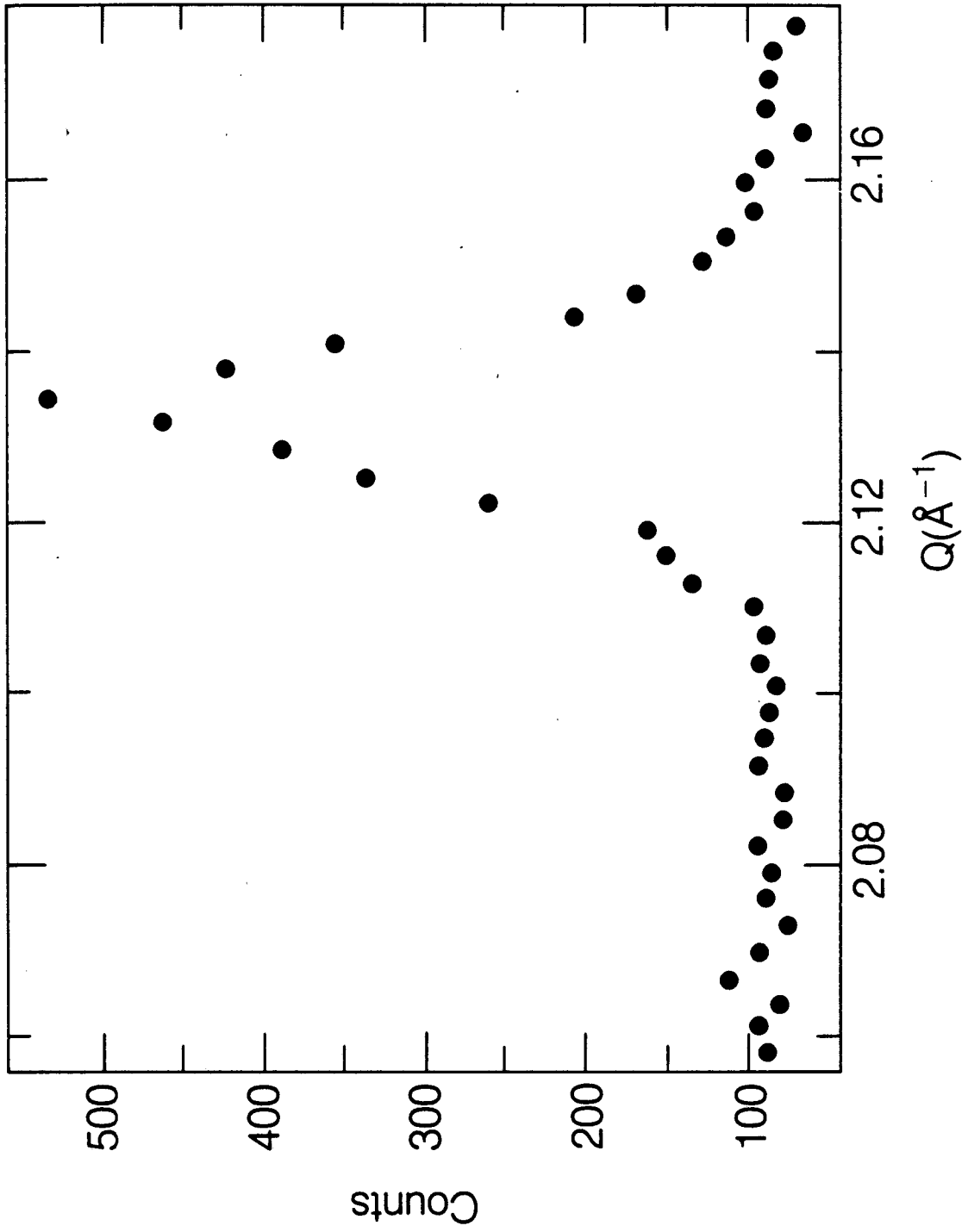
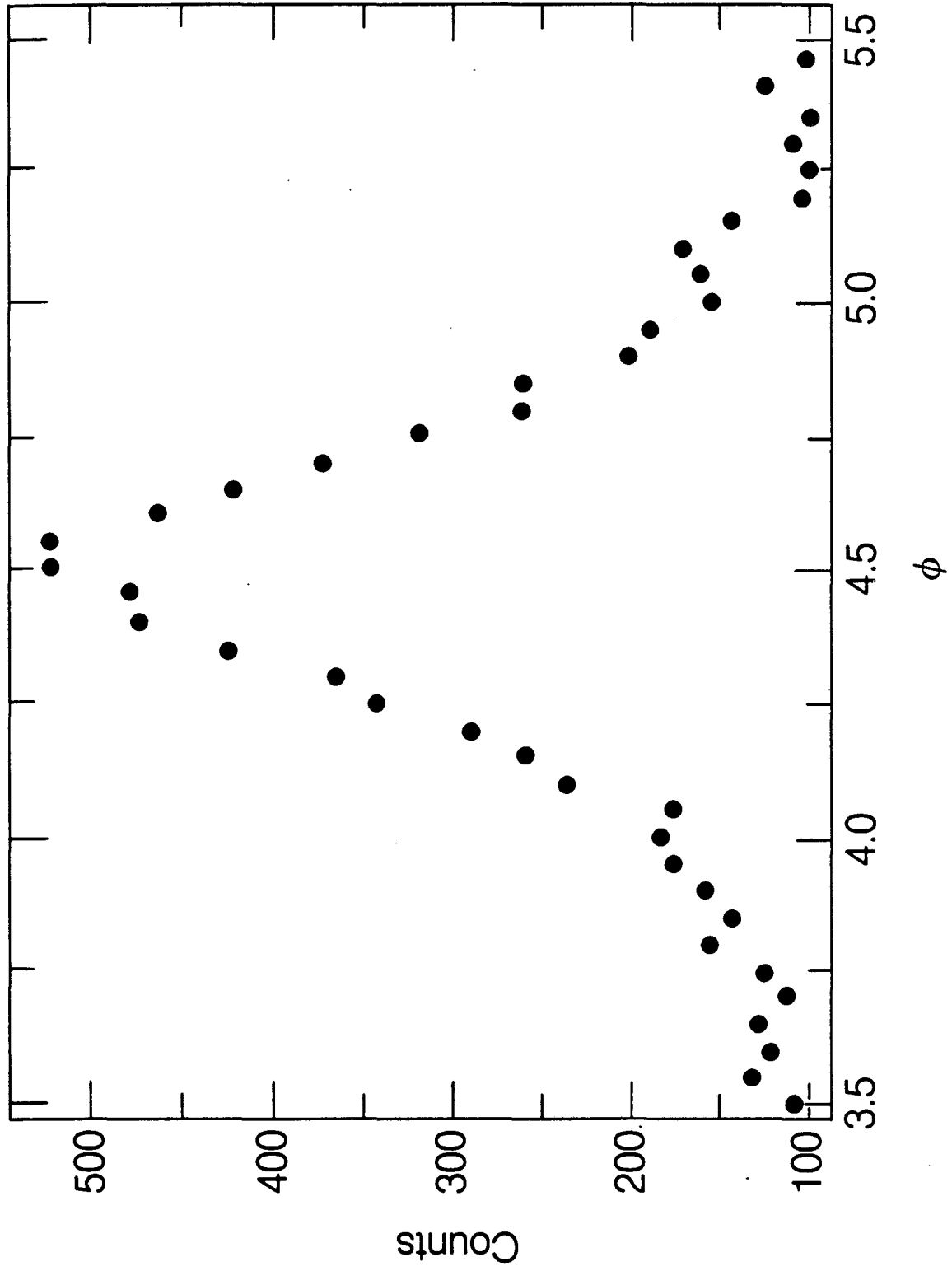


Fig. 2a

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Fig. 2b

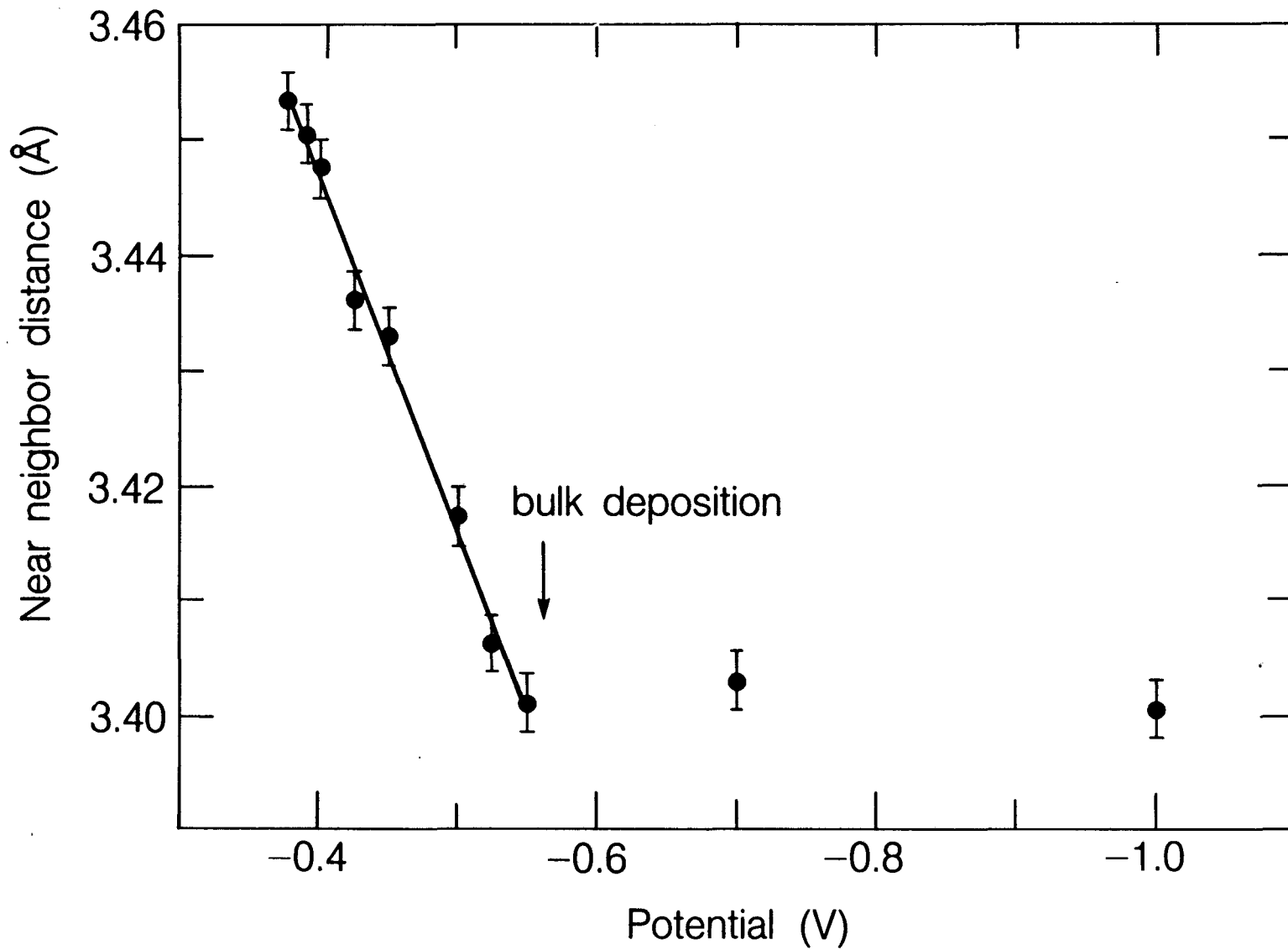


Fig. 3

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