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STUDIES OF THE MEAN DISPLACEMENT OF SURFACE ATOMS IN THE (100) AND (110) FACES OF SILVER SINGLE CRYSTALS AT LOW TEMPERATURES

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ABSTRACT

The intensities of back-diffracted low energy (10-500 eV) electrons have been measured as a function of temperature for the (110) and (100) faces of single crystal silver in the temperature range -195° to 85°C. From these data the mean displacements, $\langle u_{\perp} \rangle$, of surface atoms perpendicular to the surface planes have been calculated and the magnitude of the parallel components, $\langle u_{\parallel} \rangle$, estimated.

The perpendicular components of the surface mean displacements on silver (110) and (100) surfaces are 60% and 100% larger than those of bulk atoms. There is little difference in magnitude between the parallel and perpendicular components for these faces as has also been reported for the (111) face. In addition, the parallel components of the mean displacements did not exhibit anisotropy within the accuracy of the measurements, and the physical adsorption of several noble gases had no effect on any of these measurements. The surface mean displacement for silver and those other face centered cubic metals studied are larger than predicted by theory which assumes bulk force constants for the surface atoms. This suggests that force constants for surface atoms are smaller than those of bulk atoms.

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I. INTRODUCTION

It has long been recognized that the mean displacements of surface atoms should be different from those of bulk atoms.[1] Theoretical calculations which predict the magnitude of this difference have been reported for cubic metals,[2] ionic,[3] and molecular solids.[4] The calculations for the face-centered cubic metals indicate[5] a larger ($\approx \sqrt{2}$) mean displacement perpendicular to the surface plane ($\langle u_{\perp} \rangle$). The mean displacements in the surface plane ($\langle u_{\parallel} \rangle$) have also been calculated and found to be a function of crystal orientation. In general, these computations[2,5] make use of (1) the harmonic approximation and (2) force constants for surface atoms which are identical to those in the bulk. The larger surface mean displacements are primarily due to the change in the number of nearest neighbors for surface atoms. The mean displacements of surface atoms are measurable by low energy electron diffraction (LEED) from the single crystal surface. The temperature dependence of the different diffracted electron beam intensities [($I_{hk\ell}$) minus the background (I_0)] is measured and the Debye-Waller factor

$$\left[\frac{d \log (I_{hk\ell} - I_0)}{dT}\right]_{eV} = \text{const.}$$

is calculated from which either the effective surface mean displacement $\langle u^{eff} \rangle$ or the effective surface Debye temperature (Θ_D^{eff}) is readily obtained. Since low energy electrons (5-500 eV) back-scatter primarily from the surface, the mean displacement calculated from Debye-Waller factor measurements at low electron energies is the property of the

surface atoms. However, at higher energies a larger fraction of the diffracted electrons may penetrate into the bulk,[6] and the calculated mean displacement values should approach the bulk value.[7] Such measurements have previously been carried out using the different low index crystal faces of several face-centered cubic metals (Pt, Pd, Pb, Ag, and Ni).[6-9] For platinum,[6] palladium,[7] and lead[7] surfaces the mean displacements perpendicular to the surface plane were found to be much larger than that predicted by the theory. However, the (111) crystal face of silver showed surface mean displacements $\langle u_{\perp} \rangle$ of the magnitude predicted by the model calculations.[8] Anisotropy in the parallel mean displacements is expected for the (110) face of face-centered cubic crystals due to the asymmetry in the atomic arrangements along $[1\bar{1}0]$ and the [001] directions.[2] Such anisotropy in the mean displacements parallel to the surface plane has been reported by MacRae[9] for the Ni (110) surface.

In this study we shall attempt to elucidate the causes of the discrepancy between the experimentally observed and calculated values of the surface mean displacements for face centered cubic crystals $[\langle u \rangle_{obs} > \langle u \rangle_{calc}]$. For this purpose we have measured the perpendicular and the parallel components of the mean displacement of surface atoms in the (110) and (100) crystal faces of silver, and have extended the range of Debye-Waller factor measurements to low temperatures from -195°C to +85°C. It should be noted that hitherto, all of the surface Debye-Waller factor measurements were carried out at higher temperatures ($\geq$ 25°C). Low temperature measurements allow one to verify the theoretically predicted[5] exponential temperature dependence of the diffracted beam intensities for conditions of $T < \Theta_D$ (bulk) and to improve the accuracy of the measurements.

We find that the mean displacements parallel to the Ag (100) and Ag (110) surfaces are just as large as the mean displacements of surface atoms perpendicular to the surface. In addition, there was no detectable difference between the magnitude of the two parallel components of the surface mean displacement in the (110) face of silver. These results and those found on the other metals studied indicate that the force constants for surface atoms of most face centered cubic metals are isotropic and smaller than the force constants for bulk atoms.

II. EXPERIMENTAL

The low energy electron diffraction system of the post-acceleration type was used in these studies.[10] The single crystals of highest available purity were x-ray oriented, cut, polished, and etched.[11] The silver samples (9.5 mm diam, 1-2 mm thick disks) were mounted on a silver coated copper block which is part of the low temperature holder shown in Fig. 1. The sample can be cooled to liquid nitrogen temperature or heated to 600°C through the copper block. The holder allows one to rotate the sample 360° which is necessary for ion bombardment and for the purposes of other, auxiliary measurements.[11] A thermocouple has been attached to the copper block to determine the temperature of the specimen. The ambient pressure was in the range of 10^{-10} - 10^{-9} torr for all of the measurements. Diffraction patterns on the carefully prepared silver crystals were frequently observed immediately after pump-down and bake-out of the diffraction chamber. Ion bombardment (2×10^{-5} torr argon, 300 eV) and subsequent annealing heat treatments were used, however, to obtain a more ordered surface structure with sharper diffraction features. In the preliminary experiments with the Ag (110) surface it was found that the sample undergoes faceting in vacuum or in oxygen above 300°C.[11] This appeared to be an irreversible process which affected the Debye-Waller measurements markedly as will be discussed later. Therefore, in order to avoid such faceting the (110) crystal face was never annealed above 80°C and the intensity measurements were carried out in the temperature range -195° + 85°C. The Ag(100) surface appeared to be stable even at elevated temperatures ($\geq$ 200°C).

All of the measurements of the temperature dependence of the diffracted electron beam intensities were carried out by the transient method.[6] The silver crystal was chilled to -195°C using liquid nitrogen and the intensity of a chosen reflection (00, 01, etc.) has been monitored continuously at a given electron beam energy using a small angle spot-photometer,[12] while the crystal was cooling to liquid nitrogen temperature. The photometer output ($I_{hk\ell}$) and the thermocouple emf (T) were displayed simultaneously on an x-y recorder. A typical $I_{hk\ell}$ and I_0 vs T experimental curve is shown in Fig. 2.

We have measured the effective mean displacement which is perpendicular to the surface plane $\langle u_{\perp}^{eff} \rangle$ from the temperature dependence of the intensity of the specularly reflected electron beam (00-reflection). For these specularly reflected electrons the scattering vector, $(\vec{k} - \vec{k}_o)$, is perpendicular to the surface plane.[6] Therefore, the data yield only the vertical component of the effective displacement. The angle of incidence, ϕ, was in the range of 6°-20° with respect to the surface normal for the measurements of the properties of the (00)-reflection. We found that the measured Debye-Waller factor, using the (00)-reflection, was not independent of the angle of incidence within the accuracy of our measurements (10%) as previously discussed by Jones et al.[8] The parallel components of the effective mean displacement were measured by monitoring I(T) for the different (hkℓ) reflections for which the scattering vector subtends a well-defined angle α with the surface normal at a given beam voltage. Thus, the data yield a mean displacement which is a weighted average of the parallel and perpendicular components. From the independent determination of $\langle u_{\perp}^{eff} \rangle$ and from these data, the desired parallel

component is computed. The intensity of the fluorescent-screen background has been monitored by scanning the spot-photometer[12] about the reflection under investigation. Using the same sensitivity in monitoring the intensity of the diffraction spots, the background intensity slightly decreases with decreasing temperature. It should be noted, however, that this change was much smaller than the intensity change of the diffraction spots with temperature and thus, had little effect on the intensity measurements. The $I_{hk\ell}$-vs-T curves were measured at different electron beam energies in the range 50-300 eV. Those beam energies were selected in every case which corresponded to intensity maxima.

Finally, it should also be mentioned that the reproducibility of the low temperature measurements of this study was considerably better than those previous investigations which were carried out at high temperatures.[6-9] It appears that heating treatments which could give rise to diffusion controlled surface rearrangements (growth of ordered domains, changes in step density) are mostly responsible for the uncertainty observed in high temperature Debye-Waller factor measurements.

III. RESULTS

A. Working Equations

The Debye-Waller factor is obtained from the experimental intensity curves ($I_{hk\ell}$ vs T) by subtracting the background intensity (I_0). In this way the contribution of thermal diffuse scattering to the total intensity is removed.[6] The intensity of scattered electrons is given by the equation[2]

$$I = |F_{hk\ell}|^2 \exp[-16\pi \cos^2\phi/\lambda^2) \langle u^2_{\Delta k}\rangle \qquad (1)$$

where the exponential term is the Debye-Waller factor, λ, is the electron wavelength, ϕ is the angle of incidence of the specular electron beam with respect to the surface normal, $|F_{hk\ell}|^2$ is the scattered intensity by a rigid lattice and $\langle u^2_{\Delta k}\rangle$ is the mean square displacement in the direction of the scattering vector, $\Delta\vec{k} = \vec{k} - \vec{k}^0$. Using the harmonic oscillator model in the high temperature limit, the mean square displacement is given by[7]

$$\langle u^2_{\Delta k}\rangle = (3N\hbar^2/Mk)[T/\Theta_D^{eff})^2] \qquad (2)$$

where Θ_D^{eff} is the effective Debye temperature at the high temperature limit, M and T are the atomic weight and the temperature of the solid, respectively, N is Avogadro's number, and k and $\hbar$ are the Boltzmann and Planck constants. Combining Eqs. (1) and (2) we have

$$I_{hk\ell} = |F_{hk\ell}|^2 \exp\{-(12N\hbar^2/Mk)(\cos\phi/\lambda)^2 [T/\Theta_D^{eff})^2]\} \qquad (3)$$

The logarithm of the intensity of a given reflection $\log(I_{hk\ell}-I_0)$ plotted as a function of temperature T gives a straight line. From the slope, the effective Debye temperature or the mean effective displacement can be

calculated. Using the (00)-reflection in these measurements the mean displacement in the direction perpendicular to the surface plane, $\langle u_{\perp}^{eff} \rangle$, or the normal component of the effective Debye temperature, $\Theta_{\perp}^{eff}$, can be calculated. The use of any other reflection for the measurements will yield an effective Debye temperature Θ_D^{eff} with both parallel, $\Theta_{\parallel}^{eff}$, and perpendicular, $\Theta_{\perp}^{eff}$, components. For this case Eq. (3) may be rewritten as[8,9]

$$I_{hk\ell} = |F_{hk\ell}|^2 \exp \left\{ -(12Nh^2T/Mk\lambda^2) \left[\frac{\cos^2\phi}{\Theta_{\perp}^{eff\ 2}} + \frac{\sin^2\alpha}{\Theta_{\parallel}^{eff\ 2}} \right] \right\} \qquad (4)$$

where α is the scattering angle at which the particular reflection appears with respect to the surface normal. Thus, using the value, $\Theta_{\perp}^{eff}$, calculated from studies of the (00)-reflection, and the sum of the two components $\Theta_{\perp}^{eff}$ and $\Theta_{\parallel}^{eff}$ which is obtained from the intensity variation of other reflections through Eq. (4), the parallel component of the effective Debye temperature can readily be calculated.

It should be noted that the accuracy of the values of $\Theta_{\perp}^{eff}$ or $\langle u_{\perp}^{eff} \rangle$ is greater than that of the parallel components, $\Theta_{\parallel}^{eff}$ or $\langle u_{\parallel}^{eff} \rangle$ since they are obtained from direct measurements on the (00)-reflection. The parallel components are obtained by subtraction of two numbers of equal magnitude and therefore subject to greater uncertainty.

We have found, as in the case of other face-centered cubic crystals, that the measured values of the effective Debye temperatures were strongly dependent on the electron beam energy. It is apparent that at increasing electron energies a larger fraction of electron scatter from atomic planes below the surface plane. Therefore, in order to compute effective Debye temperature which are characteristic of surface atoms the $I_{hk\ell}$ vs. T curves obtained at the lowest beam voltages ($\leq$ 80 eV) were used. At such low energies for silver surfaces the largest fraction of the incident electrons back scatter from the surface atoms without penetrating deeper into the bulk. We have also found that in the temperature range of our study (-195° - +85°C), the log $(I-I_0)$ vs. T plots invariably gave straight lines. A typical curve for silver (110) is shown in Fig. 3. This observation is in accordance with the calculations of Wallis, et al.[5] They have concluded that the linear dependance of the mean square displacement on absolute temperature should extend to temperatures well below the bulk Debye temperature.

B. Mean Displacements in the Ag(100) Surface

The perpendicular component of the effective mean displacement, $\langle u_{\perp}^{eff} \rangle$, plotted as a function of beam voltage is shown in Fig. 4. These values were obtained from the log $(I-I_0)$ vs. T curves using Eqs. (2) and (3). It can be seen that the surface mean displacement is larger than the bulk value (dotted line) by about 100%. The effective mean displacement has reached the bulk value at electron energies $\geq$ 190 eV. It increases rapidly with decreasing electron energy, reaches a plateau between 90 - 120 eV then increases again between 57-90 eV. The rapid change in the effective mean displacement shows no sign of levelling off in the

range of the two lowest electron beam energies (57-68 eV) used in these measurements. Measurements could not be extended to even lower beam voltages due to the geometry of the low temperature holder used in these experiments.

The I vs. T curves were measured for several reflections other than the specular reflection in order to obtain the parallel components of the mean displacement. In Table I we plot the different reflections, scattering angles and electron beam energies which were used. It was found that the slopes of the log $(I-I_0)$vs. T plots obtained by monitoring the intensity change of the different $(hk\ell)$ reflections or the (00)-reflection were almost identical at a given electron beam energy, certainly indistinguishable within the accuracy of the measurements. Thus, it becomes very difficult to evaluate the parallel mean displacement (Eq. 4) with any reasonable accuracy. Variations in the small background correction could introduce large errors in the computed value of $\langle u_{\parallel}^{eff} \rangle$. Therefore, instead of reporting the parallel mean displacement for the (100) surface we give, in Table I, the slopes of the log $(I-I_0)$ vs. T plots. The parallel and perpendicular components of the effective mean displacements appear to be identical within the accuracy of the measurements. Also the slopes, obtained by monitoring the (30) and (03) reflections are nearly the same. As expected, there seems to be no detectable difference between the two components of the parallel mean displacements for the (100) orientation.

Several noble gases (xenon, argon and krypton) were introduced($\approx 10^{-6}$ torr) during the surface Debye-Waller factor measurements in order to investigate their effect, if any, on the $I_{hk\ell}$ vs. T curves. These gases are believed to physically adsorb on the Ag(100) surface in the studied temperature range

as disordered liquid-like patches.[11] The presence of these gases had no detectable effect on the temperature dependence of the intensity.

C. Mean Displacements in the Ag(110) Surface

The perpendicular component of the effective mean displacement $\langle u_{\perp}^{eff} \rangle$ and the effective Debye temperature $\Theta_{\perp}^{eff}$ for the Ag(110) orientation as a function of beam voltage is given in Fig. 5. It is apparent that the bulk values are not approached as rapidly with increasing electron beam energy as for the (100) face. There are also marked differences at low beam voltages. After an initially rapid increase of $\langle u_{\perp}^{eff} \rangle$ in the range 100-160 eV with decreasing beam voltage the change in the mean displacement levels off and remains about 50-60% higher than the bulk value. Thus the perpedicular component of the surface mean displacement is appreciably smaller for the (110) face than that for the (100) crystal face, but both are markedly larger than the bulk value.

The I vs. T curves were measured for several reflections in order to obtain both parallel components of the mean displacement. At low beam voltages($\leq$ 94 eV) the slopes, $\left[d \log(I_{hk\ell}-I_0/dT\right]_{eV=const}$ using the (20) or (02) reflections were equal to the slopes which were obtained using the specular (00) reflection. Thus, it appears, that just as in the case of the (100) and (111)[8] surfaces the mean displacements in the (110) surface are isotropic. At higher electron beam energies (> 160 eV) however, the slopes using the different (hkℓ) reflections are different from the slopes using the (00) reflection at the same scattering angle. The parallel components of the effective Debye temperatures are always somewhat smaller than the perpendicular component. This is shown in Table II. Here we list the measured reflections, scattering angles and electron energies which were

used. The effective mean displacements ($\langle u_{\perp}^{eff} \rangle$, $\langle u_{\parallel}^{eff} \rangle$) and effective Debye temperatures ($\theta_{\perp}^{eff}$, $\theta_{\parallel}^{eff}$) are also tabulated.

The parallel mean displacements were determined using both (h,0) and (0,h) reflections. Since there is an anisotropy in the crystal orientation in these two perpendicular directions a difference in the lateral mean displacements in these different directions was postulated.[2] However, we have found the parallel mean displacement to be the same in both directions within the accuracy of our experiments for all electron beam energies. Inspection of Table II also reveals that the calculated parallel mean displacement values show little angular dependence within the accuracy of our measurements. Intensity measurement at even higher beam voltages could not be carried out. The magnitude of the Debye-Waller factor and its wavelength dependence decreases the diffraction beam intensities which makes the I-vs-T measurements unreliable at higher beam voltages.

All of the results shown in Fig. 5 were obtained from silver crystals which were annealed at $T \leq 85°C$ and the Debye temperatures were obtained from measurements at low temperatures (-195° - +85°C). Different and somewhat irreproducible results were obtained when a (110) crystal was heated above 80°C to 200°C. These are shown in Fig. 6. Low energy electron diffraction and ellipsometry studies[11] have showed that the Ag(110) surface undergoes thermal faceting above 300°C, new crystal faces develop which replace the (110) orientation. Since faceting is an irreversible process it appears that the surface properties of the (110) orientation can only be studied reproducibly by low temperature measurements which were carried out in this investigation. In the same figure we also plot the perpendicular component of the effective Debye temperature

for the Ag(111) surface obtained by Jones et al.[8] and our data on the unreconstructed Ag(110) surface, for comparison.

In Table III we list the surface and bulk Debye temperatures which were obtained by these experiments. We also list all of the values which were obtained from studies on other face-centered cubic crystal surfaces such as nickel, platinum, palladium, and lead. The experimental and calculated values of the surface normal to bulk mean displacement ratios, $\langle u_{\perp}^{eff}\rangle$(surface)/$\langle u\rangle$(bulk), are also listed for easy comparison with the calculations by Wallis et al.[5]

IV. DISCUSSION

The following statements summarize some of the results obtained in the experiments and additional information which may help in their interpretation.

1. The exponential temperature dependence of the diffraction beam intensities from silver surfaces has been found to persist to -195°C, the lowest temperatures used in these experiments.

2. Calculations, within the harmonic approximation, indicate that the mean displacements of surface atoms perpendicular to the surface planes for the (100) and (110) orientations of silver crystals are larger by 100% and 60%, respectively, then the bulk value.

3. The perpendicular surface mean displacements, $\langle u_{\perp}^{eff} \rangle$, for the silver (100) and (110) crystal faces and for different crystal faces of many other face-centered cubic metals were found to be larger by experiments than that predicted by theory[5] which uses bulk force constants for the model calculations.

4. The mean displacements in the Ag(110) surface, parallel to the surface plane shows no apparent anisotropy. The displacements along the [1$\bar{1}$0] and [001] directions are equal and certainly as large as the perpendicular mean displacement within the accuracy of the measurements. There is also little difference between the parallel and perpendicular components of the mean displacements of surface atoms in the Ag(100) and Ag(111)[8] surfaces.

5. The Ag(110) face shows anomalous behavior[11] above 140°C which strongly effects the surface Debye-Waller factor measurements. Therefore,

studies on this crystal face should be carried out only at low temperatures. Our experiments, in the temperature range -195° to + 85°C have yielded reproducible results.

The low temperature studies on the clean silver single crystal surfaces indicate that the exponential temperature dependence of the diffracted beam intensities which is predicted by the simple theory[2] for high temperatures ($T > \Theta_D^{\infty}$) is obeyed down to liquid nitrogen temperature (-195°C) at any electron beam energy. This behavior was predicted by Wallis et al.[5] Therefore, we have analyzed our data using Eqs. (1) through (3) as carried out in previous high temperature experiments. In every case, the experimentally determined ratio $\langle u_{\perp}^{eff} \rangle / \langle u \rangle_{bulk}$ is larger than predicted by the theory.[5] It should be noted that the tabulated values are only lower limits to the true effective Debye temperature, for they were computed from measurements at a finite, instead of zero electron energy. Thus, they may contain contributions from atomic planes which lie below the surface plane. In their calculations, Wallis et al. have assumed interatomic coupling constants (force constants) for surface atoms which are the same as that for bulk atoms. They have indicated, however, that this assumption is most likely incorrect; in fact, by assuming a force constant for surface atoms which is one-half of that of the bulk, they have obtained good agreement with the mean displacement values measured for the Ni(1$\bar{1}$0) surface. The calculated mean displacement values were also insensitive to the inclusion of next-nearest neighbor interactions and angle-bending forces in the computations. It is also unlikely that multiple scattering effects in low energy electron diffraction[13] could be responsible for the observed larger mean displacements although they

may affect the penetration depth of the low energy electrons. All of the diffraction beams which appear in the I_0 vs. eV curves, primary or "secondary," yield effective mean displacements which fit well on the experimental curves shown in Figs. 4 and 5. In addition, similar results were obtained in studies of the surface Debye temperature of other face-centered cubic metals[6-7] which are listed in Table III. The surface mean displacement also approaches the bulk value with increasing electron energy which is determined by independent heat capacity measurements (Figs. 4 and 5). Thus, the experimental results seem to indicate that the force constants for surface atoms is markedly smaller than for atoms in the interior of the solid. The magnitude of the force constants could be obtained by judicious adjustment of their values in the model computations to fit the experimental data. They may also be readily estimated from the surface Debye temperatures using the simple relationships developed by Domb and Salter.[14]

The parallel mean displacements in the $[1\bar{1}0]$ and [001] directions were identical within the accuracy of the experiments for the silver (110) surface. This is somewhat surprising since the (110) crystal face shows marked anisotropy in these two directions. Model calculations[2] predict the parallel mean displacement in [001] direction to be the same as $\langle u_{\perp}^{eff} \rangle$ or even slightly larger and to be markedly smaller than $\langle u_{\perp}^{eff} \rangle$ in the $[1\bar{1}0]$ direction. Debye-Waller measurements on the Ni(110) surface[9] seems to have confirmed this effect qualitatively, if not its magnitude. There may be several reasons for the lack of anisotropy in the parallel mean displacements in the Ag(110) surface. 1) Changes in the force constants for surface atoms in silver may cancel out any apparent asymmetry effect.

The use of smaller force constants in the model calculations tends to minimize this anisotropy.[5] 2) The temperature dependence of dominant multiple scattering events may mask the differences between the surface mean displacement components. 3) The experiments on Ni(110) surfaces may have been affected by the possible diffusion controlled surface rearrangements, changes in step density, etc. which are precursors to faceting and seem to be unavoidable for this crystal orientation at elevated temperatures.[11] The Debye-Waller experiments on nickel surfaces were carried out in the temperature range of 100° to 600°C.[4] Finally, 4) the accuracy of our experiment may be inadequate to detect small differences in the parallel mean displacements of surface atoms in silver.

The lack of any marked dependence of the parallel mean displacements on the scattering angle indicates that the anisotropy effects may not be masked on account of the angular range used in the experiments.

The parallel and perpendicular components of the mean displacements were also equal for the Ag(100) and Ag(111) orientations.[8] This result could indicate that the force constants for surface atoms are isotropic for all crystal orientations.

It is interesting to note that the bulk mean displacement is approached with increasing electron energy more rapidly for the (100) face of silver than for the (110) or (111) face. It appears that there is a greater bulk contribution to the measured effective mean displacement at a given electron beam energy along the [100] axis than along other crystallographic directions. This is contrary to observations for other face centered cubic metals for which the effective mean displacements changes most rapidly with electron energy along the [111] direction.[6,7] However, silver

appears to be different from other face centered cubic metals in the fact that the surface mean displacement, $\langle u_{\perp}^{eff} \rangle$, in the Ag(100) orientation is markedly larger than the (110) or (111) directions. For the other metals which were studied $\langle u_{\perp}^{eff} \rangle$ is relatively insensitive to changes of crystal orientation or surface density.[6,7] It is likely that differences in net displacements along the different crystal orientations could markedly influence both, the observed effective mean displacements and the change of the effective mean displacements with beam voltage. Calculations by Burton and Jura[15] for several face centered cubic metals indicate different net displacements for the (100), (110) and (111) surfaces for silver (6.4%, 4.7% and 1.9%, respectively).

Weakly adsorbed noble gases had no effect on the surface Debye-Waller measurements. It is apparent that physical adsorption does not detectably affect the anisotropy of the surface environment. This is to be compared with results obtained during the chemisorption of several gases on tungsten surfaces[16] where due to the formation of strong chemical bonds the surface Debye-Waller factor changes markedly.

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Table I. The slopes of the log $(I-I_0)$ vs. T curves, the effective Debye temperatures calculated for Ag(100) at different reflections, scattering angles and electron beam energies.

Reflection	eV	ϕ	α	$\theta_{\perp}$ (°K)	slope ($\perp$)	slope ($\parallel$)
(30)	103	0°	31.13°	—	—	5.86×10^{-3}
(03)	103	0°	31.13°	—	—	6.42×10^{-3}
(30)	73	0°	33.87°	—	—	7.0×10^{-3}
(00)	103	16.6°	0°	146°	6.35×10^{-3}	—
(00)	103	16.6°	0°	146°	6.35×10^{-3}	—
(00)	73	16.6°	0°	125°	6.21×10^{-3}	—

Table II. The effective mean displacements and Debye temperatures for the Ag(110) surface calculated at different reflections, scattering angles and electron beam energies.

Reflection	eV	α	$\Theta_{\parallel}^{eff}$ (°K)	$\langle u_{\parallel}^{eff} \rangle$ [a] (Å)	Reflection	eV	ϕ	$\Theta_{\perp}^{eff}$ (°K)	$\langle u_{\perp}^{eff} \rangle$ [b] (Å)
(40)	195	38.4°	159	0.126	(00)	195	19.2°	196	0.103
(04)	195	38.4°	138	0.146	(00)	195	19.2°	196	0.103
(30)	195	27.2°	113	0.178	(00)	195	19.2°	196	0.103
(30)	160	29.7°	111	0.181	(00)	160	17.1°	192	0.105
(03)	164	25.4°	121	0.166	(00)	164	13.8°	193	0.104

[a] Average $\langle \bar{u}_{\parallel}^{eff} \rangle = .151$ (Å)

[b] Average $\langle \bar{u}_{\perp}^{eff} \rangle = .104$ (Å)

Table III. Surface to bulk mean displacement ratios (experimental and theoretical), surface and bulk Debye temperatures for Pd, Pb, Pd, Ag, and Ni.

Metal	$\left.\frac{\langle u_\perp^{eff}\rangle}{\langle u\rangle(\text{bulk})}\right\|_{exp}$	$\left.\frac{\langle u_\perp\rangle}{\langle u\rangle(\text{bulk})}\right\|_{calc.}$	$\theta_\perp^{eff}$ (°K)	θ_D(bulk) (°K)
Pd[7] (100), (111)	1.95	1.41	140	273
Pb[7] (111)	1.64	1.41	55	90
Pt[6] (100),(110),(111)	2.12	1.41	110	234
Ag[8] (111) This work	1.46	1.41	155	225
Ag (110) This work	1.48	1.41	152	225
Ag (100) This work	2.16	1.41	104	225
Ni[9] (110)	1.77	1.41	220	390

FIGURE CAPTIONS

Fig. 1 Low temperature manipulator

Fig. 2 (b) $I_{hk\ell}$ vs. T for silver (110)

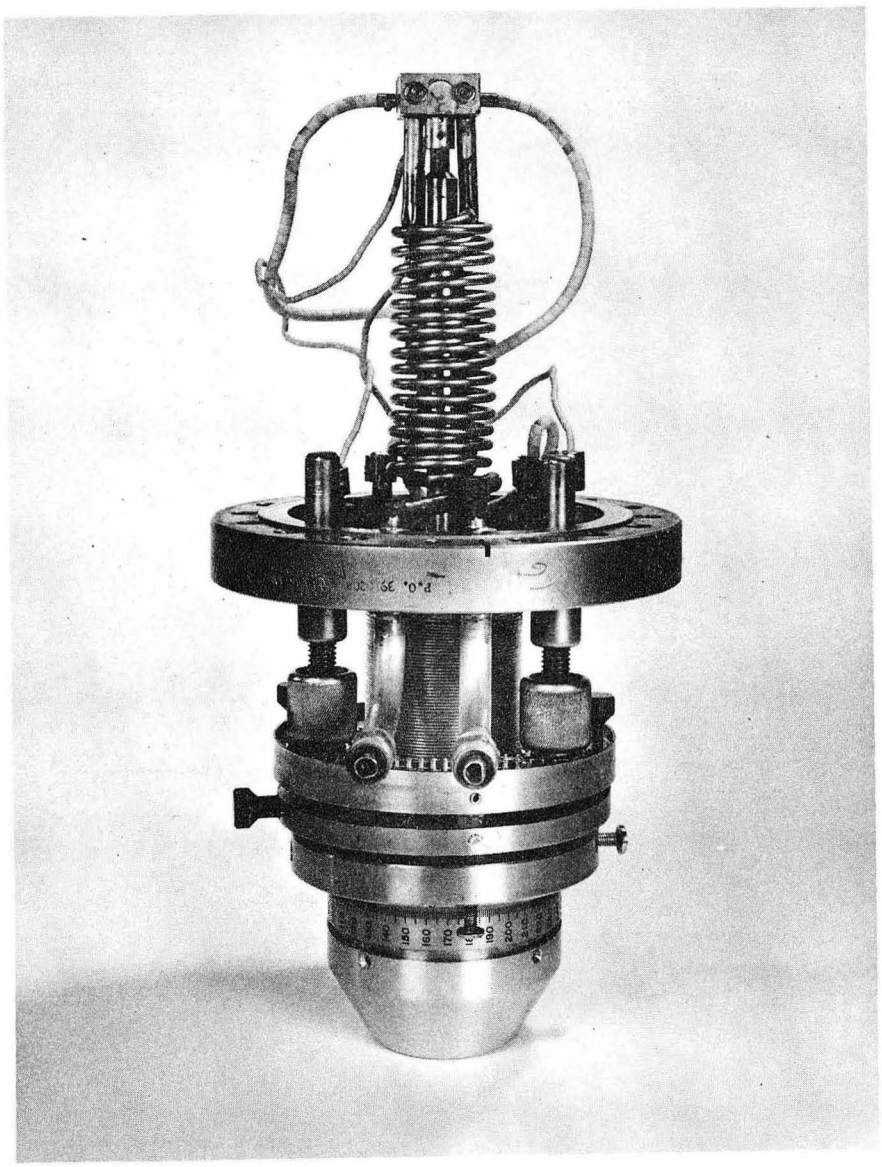
(a) I_0 vs. T for silver (110)

Fig. 3 log $(I_{hk\ell}-I_0)$ vs. T for silver (110)

Fig. 4 $\Theta_{\perp}^{eff}$(°K) and $\langle u_{\perp}^{eff}\rangle$(Å) plotted as a function of beam voltage (eV) for silver (100). Error on $\Theta_{\perp}^{eff}$ indicated by vertical line. Θ_{bulk} and $\langle u_{bulk}\rangle$ also indicated by the dashed lines.

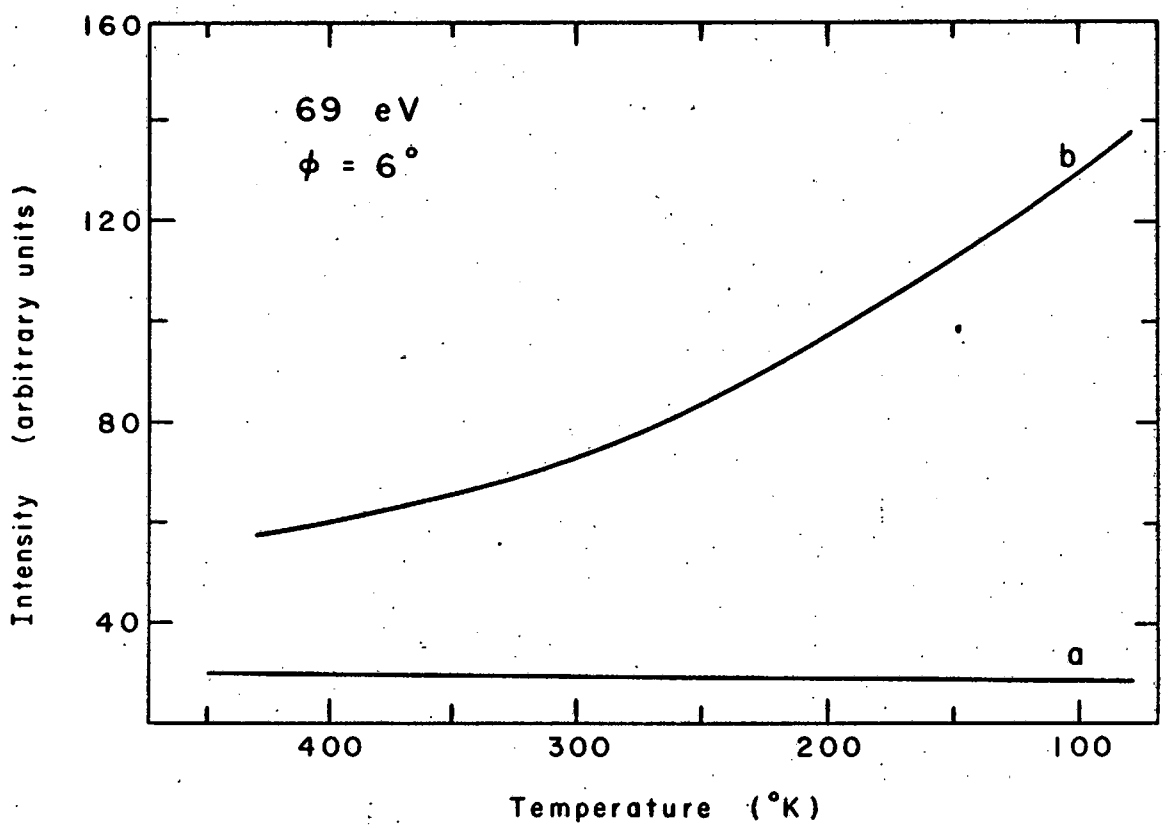
Fig. 5 $\Theta_{\perp}^{eff}$(°K) and $\langle u_{\perp}^{eff}\rangle$(Å) plotted as a function of beam voltage (eV) for silver (110). Error on $\Theta_{\perp}^{eff}$ indicated by vertical line. Θ_{bulk} and $\langle u_{bulk}\rangle$ also indicated by the dashed lines.

Fig. 6 Surface Debye temperatures for a silver (110) face after different surface treatments, indicating precursor to faceting due to heating above 140°C. Broken line literature data for (111) face.[8]



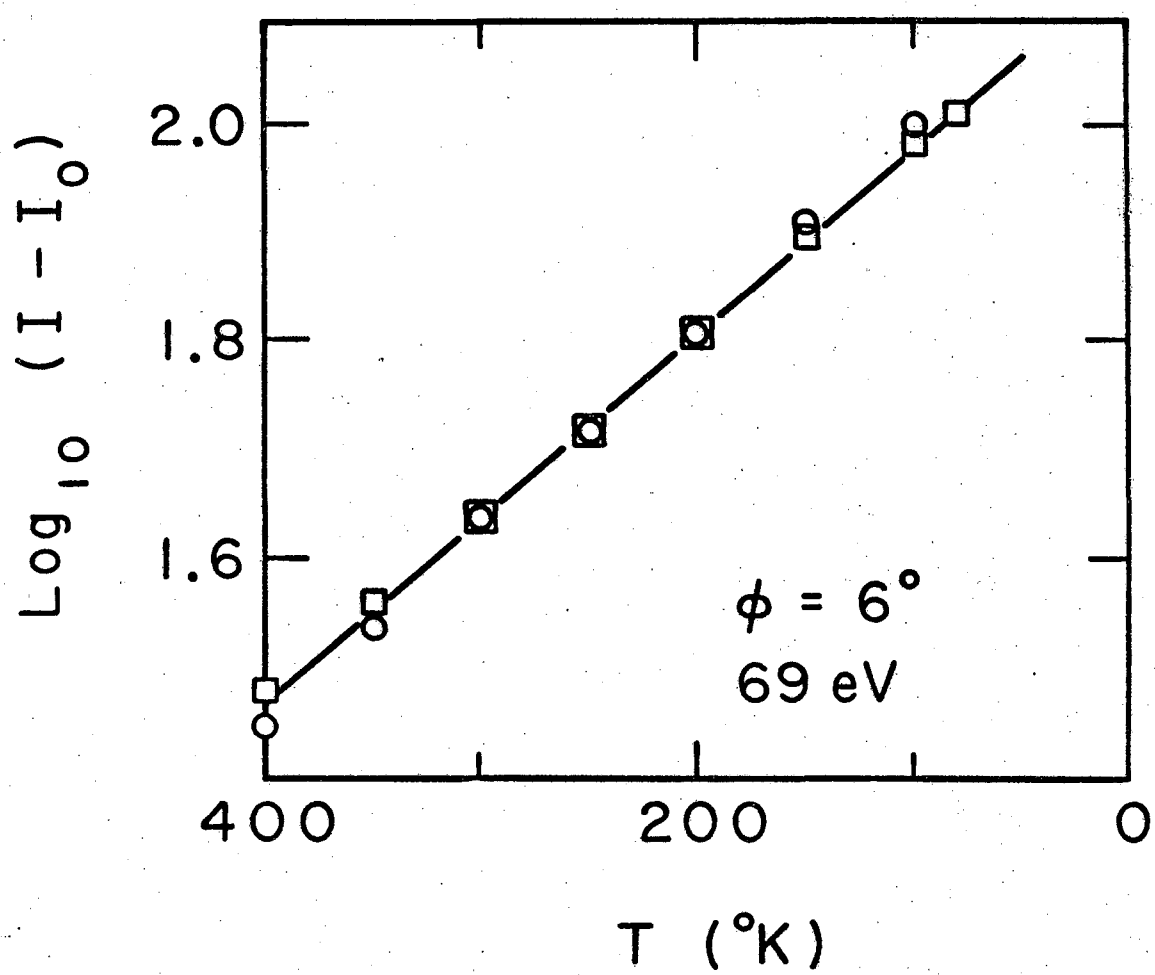
XBB 681-377

Fig. 1



XBL689-3893

Fig. 2



XBL689-3889

Fig. 3

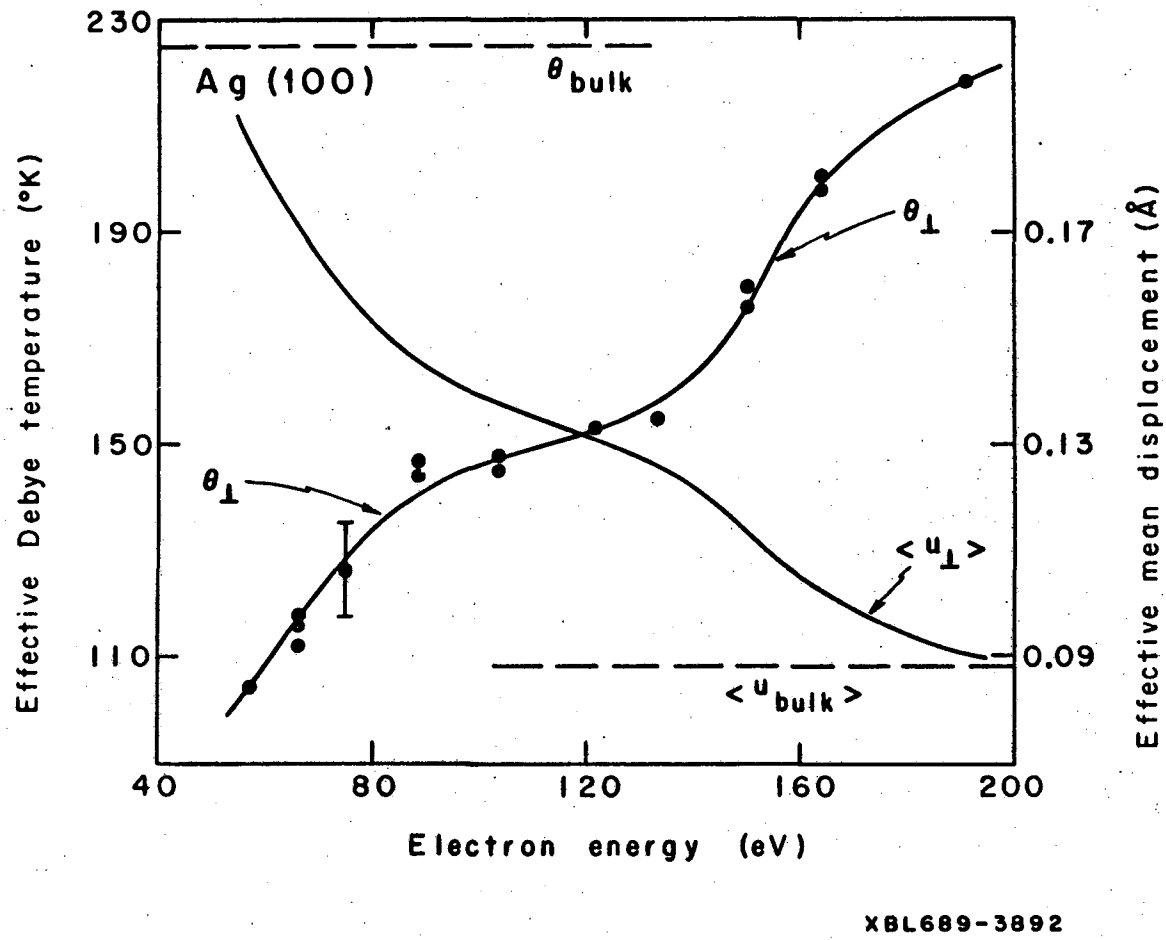

Ag (100)
θbulk
θ⊥
θ⊥
<u⊥>
<ubulk>
230
190
150
110
0.17
0.13
0.09
40
80
120
160
200
Effective Debye temperature (°K)
Effective mean displacement (Å)
Electron energy (eV)
XBL689-3892

Fig. 4

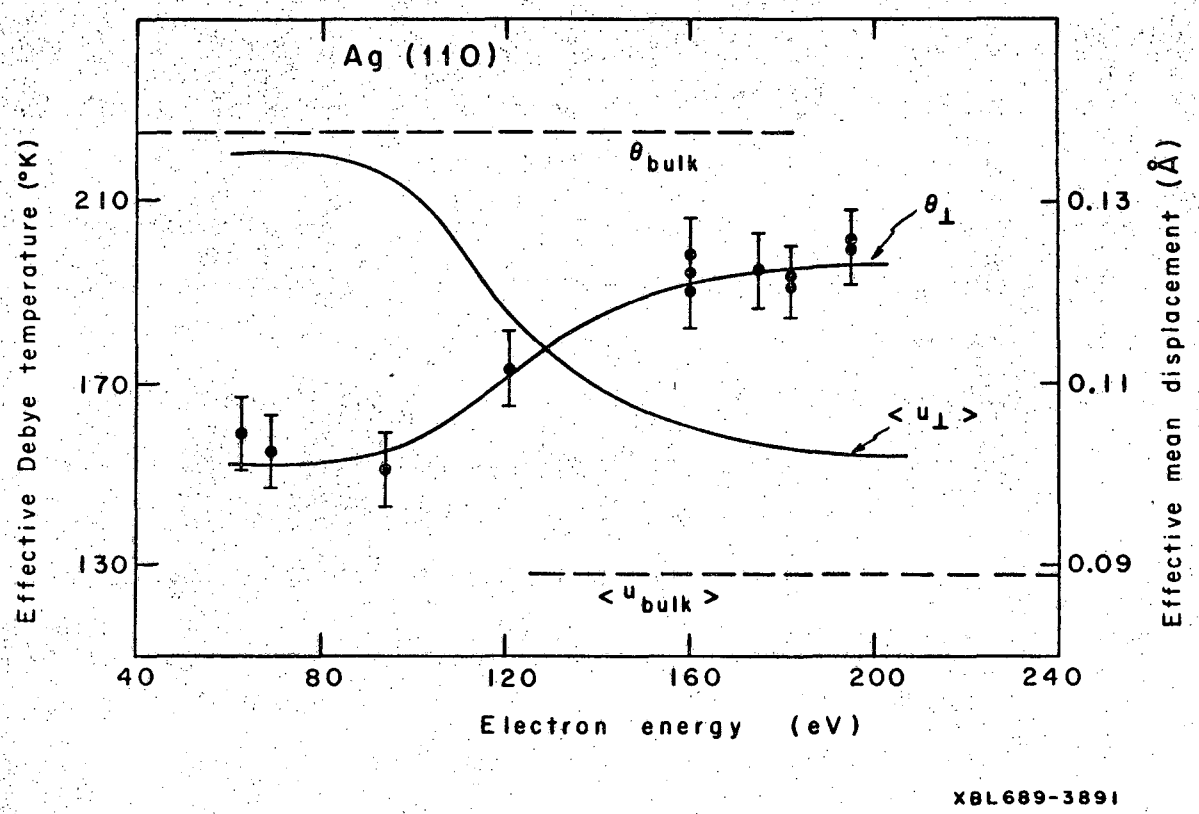
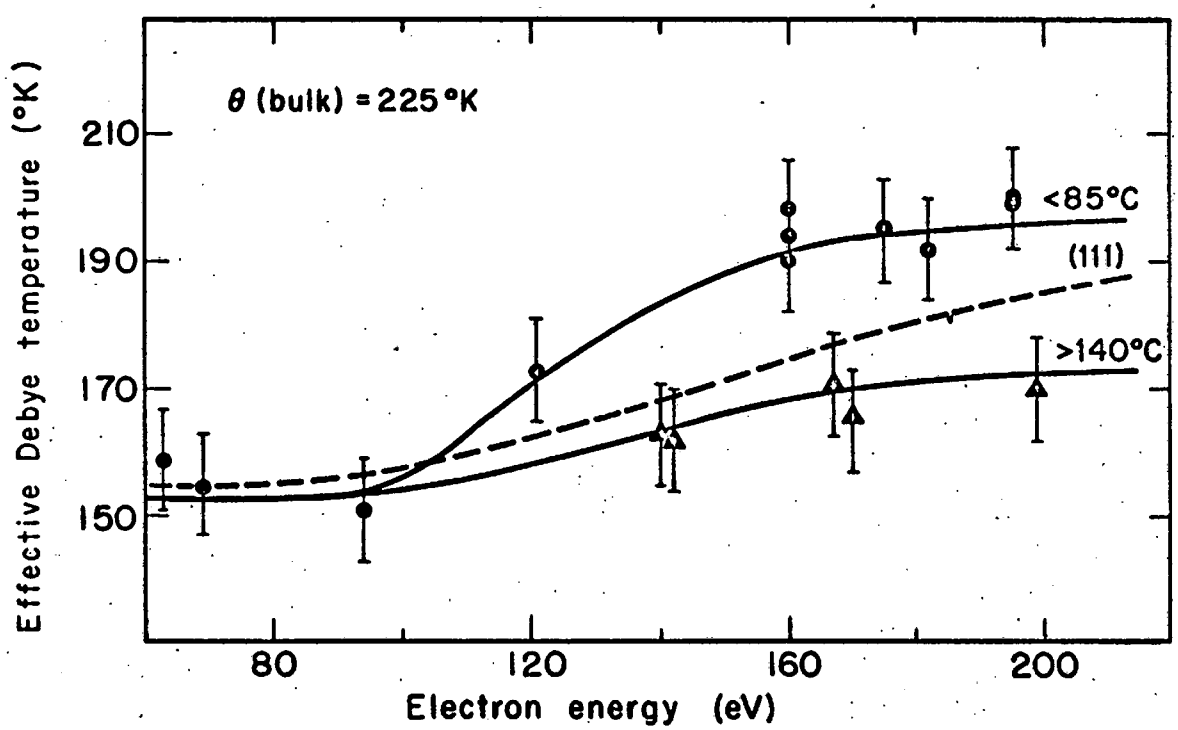

Ag (110)
θ_{bulk}
$\theta_{\perp}$
$\langle u_{\perp} \rangle$
$\langle u_{bulk} \rangle$
Effective Debye temperature (°K)
Effective mean displacement (Å)
210
170
130
0.13
0.11
0.09
40
80
120
160
200
240
Electron energy (eV)
XBL689-3891

Fig. 5



XBL 687-3390-A

Fig. 6

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