

before breaking. In comparison, the change in magneto-resistance for Li is less than 0.5% per percent strain after the phase transformation has been completed. No linear magneto-resistance has been observed in Li. The results were repeatable.

These results differ from those of Penz and Bowers¹ for K in sign, although the magnitude is about the same.

There are several differences between the experiments which may account for the result. It is unlikely that the sample geometry or the method of measurement seriously affects the result in view of the consistency of the unstrained data. The (initially) single crystals of Ref. 1 were almost certainly polycrystalline after the initial strain. The helicon method measures the averaged transverse magneto-resistance rather than the longitudinal effect.

The helicon method of straining is compressional rather than extensional, and the geometry is such that during the strain the ends of the flat plate are relatively constrained; thus the flow may be rather complex, whereas for the wire the sides are unconstrained. The strains were performed at 77°K for the helicon method and at 4.2°K for the wires. There is evidence for annealing at very low temperatures for the alkali metals.⁵

By comparing the effects in Na, K, and Li, we conclude that Na and K have an extra contribution to the magneto-resistance which is linear in magnetic field and is affected by strain. The sign of the strain dependence depends on the nature of the strain. A relatively indirect mechanism may be the explanation.⁶

⁵ D. Guban, *Phil. Mag.* **13**, 533 (1966).

⁶ J. R. Reitz and A. W. Overhauser, *Phys. Rev.* **171**, 749 (1968).

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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The intensities of back-diffracted low-energy (10–300-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 rms displacements (u_{\perp}) of surface atoms perpendicular to the surface planes have been calculated and the magnitudes of the parallel components (u_{\parallel}) estimated. The perpendicular components of the surface rms 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. The parallel components of the rms 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 rms displacement for silver and those other fcc 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.

I. INTRODUCTION

IT has long been recognized that the rms 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

indicate⁵ a larger ($\approx\sqrt{2}$) rms displacement perpendicular to the surface plane ($\langle u_{\perp} \rangle$). The rms 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 (a) the harmonic approximation and (b) force constants for surface atoms which are identical to those in the bulk. The larger surface rms displacements are primarily due to the change in the number of nearest neighbors for surface atoms. The rms 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_{hkl} minus the background (I_0)] at the beam

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¹ E. W. Montroll, *J. Chem. Phys.* **18**, 183 (1950).

² B. C. Clark, R. Herman, and R. F. Wallis, *Phys. Rev.* **139**, A860 (1955).

³ G. C. Benson, P. T. Freeman, and E. Dempsey, *J. Chem. Phys.* **39**, 302 (1963).

⁴ B. J. Alder, J. R. Vaisnys, and G. Jura, *J. Phys. Chem. Solids* **11**, 182 (1959).

⁵ R. F. Wallis, in *The Structure and Chemistry of Solid Surfaces*, edited by G. A. Somorjai (John Wiley & Sons, Inc., New York, 1969), Chap. 17.

energy E_0 is measured, and the Debye-Waller factor

$$\left[\frac{d \ln(I_{hkl} - I_0)}{dT} \right]_{E_0 = \text{const}}$$

is calculated from which either the effective surface rms displacement (u^{eff}) 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 rms 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 rms displacement values should approach the bulk value.⁷ Such measurements have previously been carried out using the different low-index crystal faces of several fcc metals (Pt, Pd, Pb, Ag, and Ni).^{6–9} For platinum,⁶ palladium,⁷ and lead⁷ surfaces, the rms 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 rms displacements (u_{\perp}) of the magnitude predicted by the model calculations.⁸ Anisotropy in the parallel rms displacements is expected for the (110) face of fcc crystals due to the asymmetry in the atomic arrangements along $[1\bar{1}0]$ and the $[001]$ directions.² Such anisotropy in the rms displacements parallel to the surface plane has been reported by MacRae⁹ 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 rms displacements for fcc crystals [$\langle u \rangle_{\text{obs}} > \langle u \rangle_{\text{calc}}$]. For this purpose we have measured the perpendicular and estimated the parallel components of the rms 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 to $+85^\circ\text{C}$. It should be noted that, hitherto, all of the surface Debye-Waller-factor measurements were carried out at higher temperatures ($\geq 25^\circ\text{C}$). Low-temperature measurements allow one to verify the theoretically predicted⁵ exponential temperature dependence of the diffracted beam intensities for conditions of $T < \Theta_D(\text{bulk})$ and to improve the accuracy of the measurements. We find that the rms displacements in the Ag (110) and Ag (100) surfaces are 60 and 100% larger than those of bulk atoms. In addition, there was no detectable difference between the magnitude of the two parallel components of the surface rms displacement in the (110) face of silver. These results and those found on the

⁶ H. B. Lyon and G. A. Somorjai, *J. Chem. Phys.* **44**, 3707 (1966).

⁷ R. M. Goodman, H. H. Farrell, and G. A. Somorjai, *J. Chem. Phys.* **48**, 1046 (1968).

⁸ E. R. Jones, J. T. McKinney, and M. B. Webb, *Phys. Rev.* **151**, 476 (1966).

⁹ A. U. McRae, *Surface Sci.* **2**, 522 (1964).

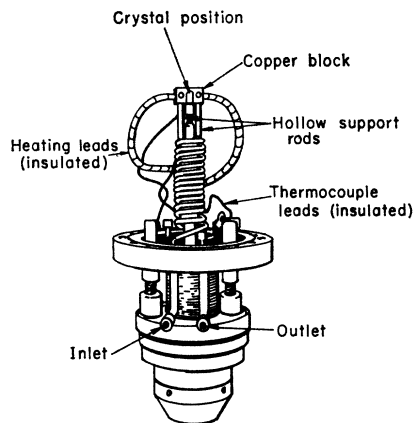


FIG. 1. Low-temperature crystal holder.

other metals studied indicate that the force constants for surface atoms of most fcc metals are smaller than the force constants for bulk atoms.

II. EXPERIMENTAL

The LEED 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 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 85°C and the intensity measurements were carried out in the temperature range -195 to $+85^\circ\text{C}$. The Ag (100) surface appeared to be stable even at elevated temperatures ($\geq 200^\circ\text{C}$).

¹⁰ LEED system by Varian Associates, Palo Alto, Calif.

¹¹ R. F. Steiger, J. M. Morabito, Jr., G. A. Somorjai, and R. H. Muller, *Surface Sci.* (to be published).

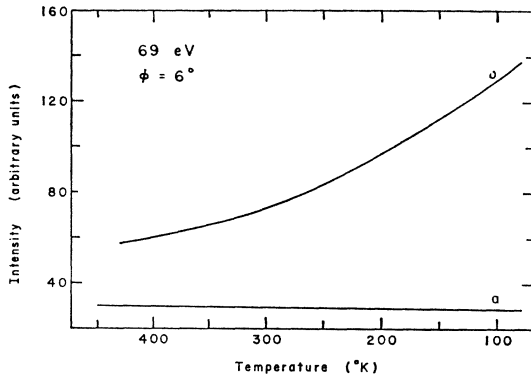


FIG. 2. (a) I_0 versus T for Ag (110) face. (b) I_{hkl} versus T for Ag (110) face.

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_{hkl}) and the thermocouple emf (T) were displayed simultaneously on an X - Y recorder. A typical I_{hkl} and I_0 -versus- T experimental curve is shown in Fig. 2.

We have measured the effective rms displacement which is perpendicular to the surface plane (u_{\perp}^{eff}) from the temperature dependence of the intensity of the specularly reflected electron beam (00 reflection). For these specularly reflected electrons, the scattering vector ($\mathbf{k}-\mathbf{k}_0$) 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, and was not independent of the angle of incidence as previously discussed by Jones *et al.*⁸ The small angular variation of the Debye-Waller factor is most likely due to the changing penetration depth of the electron beam with the incident angle. The parallel components of the effective rms displacement can be 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 (u_{\perp}^{eff}) and from these data, the desired parallel component may be computed. The intensity of the fluorescent screen background has been monitored by scanning the spot photometer¹² 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_{hkl} -versus- 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 and 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_{hkl} versus 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 by²

$$I = |F_{hkl}|^2 [\exp(-16\pi^2 \cos^2\phi/\lambda^2) \langle u_{\Delta k}^2 \rangle], \quad (1)$$

where the exponential term is the Debye-Waller factor, λ is the electron wavelength, ϕ is the angle between the incident beam of wave vector \mathbf{k} and the scattered beam of wave vector $\mathbf{k}-\mathbf{k}_0$, $|F_{hkl}|^2$ is the scattered intensity by a rigid lattice, and $\langle u_{\Delta k}^2 \rangle$ is the mean-square displacement in the direction of the scattering vector $\Delta\mathbf{k} = \mathbf{k} - \mathbf{k}_0$. It should be noted that for the specular (00 reflection) electron beam the scattering vector $\Delta\mathbf{k}$ is always normal to the surface plane. Using the harmonic-oscillator model in the high-temperature limit, the mean-square displacement is given by⁷

$$\langle u_{\Delta k}^2 \rangle = (3N\hbar^2/Mk) [T/(\Theta_D^{\text{eff}})^2], \quad (2)$$

where Θ_D^{eff} is the effective Debye temperature at the

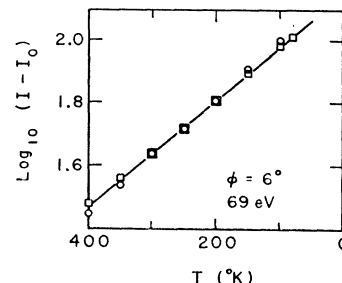


FIG. 3. $\ln(I_{hkl} - I_0)$ versus T for Ag (110) face.

¹² Telephotometer Model 2000, Gamma Scientific Instruments, San Diego, Calif.

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 h are the Boltzmann and Planck constants. Combining Eqs. (1) and (2), we have

$$I_{hkl} = |F_{hkl}|^2 \left\{ \exp \left[- (12Nh^2/Mk) \times (\cos\phi/\lambda)^2 (T/\Theta_D^{\text{eff}})^2 \right] \right\}. \quad (3)$$

The logarithm of the intensity of a given reflection, $\ln(I_{hkl}-I_0)$, plotted as a function of temperature T gives a straight line. From the slope, the effective Debye temperature or the rms effective displacement can be calculated. Using the (00) reflection in these measurements, the rms displacement in the direction perpendicular to the surface plane (u_{\perp}^{eff}), or the normal component of the effective Debye temperature $\Theta_{\perp}^{\text{eff}}$, can be calculated. The use of any other reflection for the measurements will yield Θ_D^{eff} with both parallel, $\Theta_{\parallel}^{\text{eff}}$, and perpendicular, $\Theta_{\perp}^{\text{eff}}$, components. For this case, Eq. (3) may be rewritten as⁸

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

where α is the angle between the particular reflection of scattering vector $\mathbf{k}-\mathbf{k}^0$ and the surface normal. Thus, using the value $\Theta_{\perp}^{\text{eff}}$, calculated from studies of the (00) reflection, and the sum of the two components $\Theta_{\perp}^{\text{eff}}$ and $\Theta_{\parallel}^{\text{eff}}$, which is obtained from the intensity variation of other reflections through Eq. (4), the parallel component of the effective Debye temperature may be calculated.

It should be noted that the accuracy of the values of $\Theta_{\perp}^{\text{eff}}$ or $\langle u_{\perp}^{\text{eff}} \rangle$ is much greater than that of the parallel components $\Theta_{\parallel}^{\text{eff}}$ or $\langle u_{\parallel}^{\text{eff}} \rangle$ 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 are therefore subject to greater uncertainty.

We have found, as in the case of other fcc 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 electrons scatter from atomic planes below the surface plane. Therefore, in order to compute effective Debye temperatures which are characteristic of surface atoms the I_{hkl} -versus- T curves obtained at the lowest beam voltages (≤ 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 to $+85^\circ\text{C}$) the $\ln(I-I_0)$ -versus- T plots invariably gave straight lines. A typical curve for Ag (110) is shown in Fig. 3. This observation is in accordance with the calculations of Wallis *et al.*⁵ They have

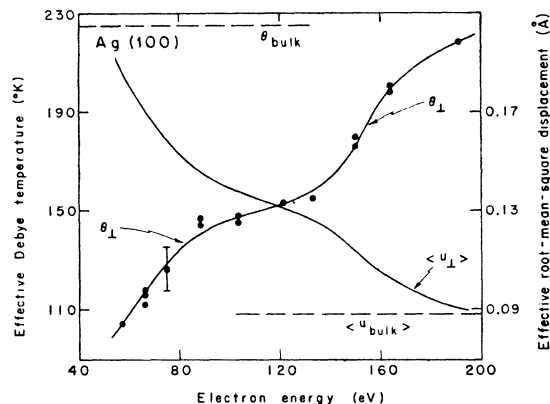


FIG. 4. $\Theta_{\perp}^{\text{eff}}$ ($^{\circ}\text{K}$) and $\langle u_{\perp}^{\text{eff}} \rangle$ (\AA) plotted as a function of beam energy for Ag (100). Error on $\Theta_{\perp}^{\text{eff}}$ indicated by vertical line. Θ_{bulk} and $\langle u_{\text{bulk}} \rangle$ also indicated by the dashed lines.

concluded that the linear dependence of the rms displacement on absolute temperature should extend to temperatures well below the bulk Debye temperature.

B. Root-Mean-Square Displacements in the Ag (100) Surface

The perpendicular component of the effective rms displacement ($\langle u_{\perp}^{\text{eff}} \rangle$) plotted as a function of beam energy is shown in Fig. 4. These values were obtained from the $\ln(I-I_0)$ -versus- T curves using Eqs. (2) and (3). It can be seen that the surface rms displacement is larger than the bulk value (dashed line) by about 100%. The effective rms displacement has reached the bulk value at electron energies ≥ 190 eV. It increases rapidly with decreasing electron energy, reaches a plateau between 90–120 eV, and then increases again between 57–90 eV. The rapid change in the effective rms displacement shows no sign of leveling 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 because of the geometry of the low-temperature holder used in these experiments.

The I -versus- T curves were measured for reflections other than the specular reflection in order to obtain the parallel components of the rms displacement. It was found that the slopes of the $\ln(I-I_0)$ -versus- T plots obtained by monitoring the intensity change of the different (hkl) 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 rms displacement [Eq. (4)] with any reasonable accuracy. Variations in the small background correction or small angular variation of the Debye-Waller factor from the (00) reflection could introduce large errors in the computed value of $\langle u_{\parallel}^{\text{eff}} \rangle$. Therefore, instead of reporting the parallel rms displacement for

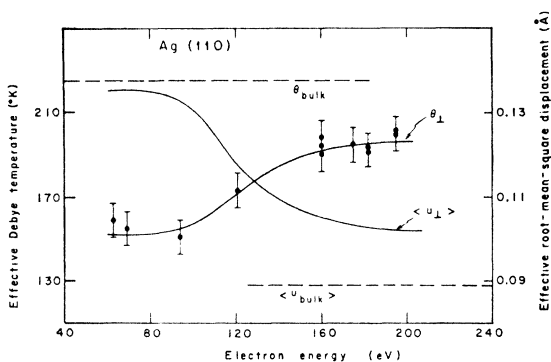


FIG. 5. Θ_1^{eff} ($^{\circ}\text{K}$) and $\langle u_1^{\text{eff}} \rangle$ (\AA) plotted as a function of beam energy for Ag (110). Θ_{bulk} and $\langle u_{\text{bulk}} \rangle$ also indicated by the dashed lines.

the (100) surface, we give in Table I the slopes of the $\ln(I-I_0)$ -versus- T plots. The parallel and perpendicular components of the effective rms 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 rms 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_{hkl} -versus- T curves. These gases are believed to physically adsorb on the Ag (100) surface in the studied temperature range as disordered liquidlike patches.¹¹ The presence of these gases had no detectable effect on the temperature dependence of the intensity.

C. Root-Mean-Square Displacements in the Ag (110) Surface

The perpendicular component of the effective rms displacement $\langle u_1^{\text{eff}} \rangle$ and the effective Debye temperature Θ_1^{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 $\langle u_1^{\text{eff}} \rangle$ in the range 100–160 eV with decreasing beam voltage, the change in the rms displacement levels off and remains about 50–60% higher than the bulk value. 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 -versus- T measurements unreliable at higher beam voltages. Thus, the perpendicular component of the surface mean displacement is appreciably smaller for the (100) face than that for the (100) crystal face, but both are markedly larger than the bulk value.

The effective rms displacements were determined using (2,0), (3,0), (4,0) and (0,2), (0,3), (0,4) reflections. Since there is an anisotropy in the crystal orientation in these two perpendicular directions, a difference in the lateral rms displacements in these different directions was postulated.² However, we have found that the slopes, $[d \ln(I_{hkl}-I_0)/dT]_{E_0=\text{const}}$, are the *same* using the $(h,0)$ or $(0,k)$ reflections and were equal to the slopes which were obtained using the specular (00) reflection within the accuracy of our experiments for all electron beam energies.

All of the results shown in Fig. 5 were obtained from silver crystals which were annealed at $T \leq 85^{\circ}\text{C}$ and the Debye temperatures were obtained from measurements at low temperatures (-195 to $+85^{\circ}\text{C}$). Different and somewhat irreproducible results were obtained when a (110) crystal was heated from 80 to 200°C . These are shown in Fig. 6. LEED and ellipsometry studies¹¹ have showed that the Ag (100) surface undergoes thermal faceting above 300°C , i.e., 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 Fig. 6, 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 II 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 fcc crystal surfaces such as Ni, Pt, Pd, and Pb. The experimental and calculated values of the surface normal to bulk rms displacement ratios, $\langle u_1^{\text{eff}} \rangle(\text{surface})/\langle u \rangle(\text{bulk})$, 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

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

Reflection	E_0 (eV)	ϕ (deg)	α (deg)	Θ_1 ($^{\circ}\text{K}$)	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}	...

been found to persist to -195°C , the lowest temperatures used in these experiments.

(2) Calculations within the harmonic approximation indicate that the rms 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, than the bulk value.

(3) The perpendicular surface rms displacements $\langle u_{\perp}^{\text{eff}} \rangle$ for the Ag (100) and (110) crystal faces and for different crystal faces of many other fcc metals were found to be larger by experiments than predicted by theory⁵ which uses bulk force constants for the model calculations.

(4) The rms displacements in the Ag (110) surface parallel to the surface plane shows no apparent anisotropy. The displacements along the $[110]$ and $[001]$ directions are equal within the accuracy of the measurements. There is also little measurable difference between the parallel and perpendicular components of the rms displacements of surface atoms in the Ag (100) and Ag (111)⁸ surfaces.

(5) The Ag (110) face shows anomalous behavior¹¹ above 140°C which strongly affects 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 $+85^{\circ}\text{C}$ 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 theory² 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)–(3) as carried out in previous high-temperature experiments. In every case, the experimentally determined ratio $\langle u_{\perp}^{\text{eff}} \rangle / \langle u \rangle_{\text{bulk}}$ is larger than predicted by the theory.⁵ It should be noted that the tabulated values

TABLE II. Surface to bulk rms displacement ratios (experimental and theoretical), and surface and bulk Debye temperatures for Pd, Pb, Pt, Ag, and Ni.

Metal	$\frac{\langle u_{\perp}^{\text{eff}} \rangle}{\langle u \rangle_{\text{bulk}}}$	$\frac{\langle u_{\perp} \rangle}{\langle u \rangle_{\text{bulk}}}$	Θ_D^{eff} ($^{\circ}\text{K}$)	$\Theta_D(\text{bulk})$ ($^{\circ}\text{K}$)
	expt	calc		
Pd ^a (100), (111)	1.95	1.51	140	273
Pb ^a (111)	1.64	1.41	55	90
Pt ^b (100), (110), (111)	2.12	1.41	110	234
Ag ^c (111)	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 ^d (110)	1.77	1.41	220	390

^a Reference 7. ^b Reference 6. ^c Reference 8. ^d Reference 9.

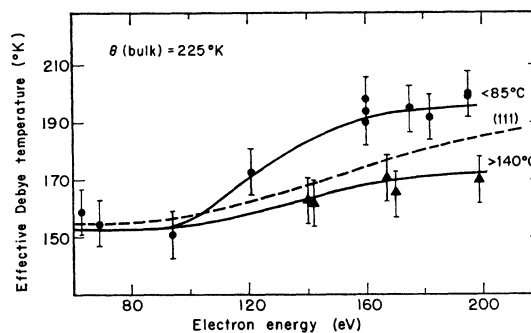


Fig. 6. Surface Debye temperatures as a function of electron energy (eV) for an Ag (110) face after different surface treatments, indicating precursor to faceting due to heating above 140°C . Dashed line indicates surface Debye temperatures for (111) face (Ref. 8).

are only upper limits to the true effective-surface 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 those 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 rms displacement values measured for the Ni (110) surface. The calculated rms displacement values were 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 LEED¹⁸ could be responsible for the observed larger rms displacements although they may affect the penetration depth of the low-energy electrons. All of the diffraction beams which appear in the I_0 -versus-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 fcc metals⁶⁻⁷ which are listed in Table II. The surface rms 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

¹⁸ R. M. Stern, in Proceedings of Symposium on Low-Energy Electron Diffraction, 1968 (unpublished).

¹⁴ C. Domb and L. Salter, Proc. Roy. Soc. (London) **133**, 1083 (1953).

The parallel rms displacements in the $[\bar{1}\bar{1}0]$ and $[001]$ directions were identical within the accuracy of the experiments for the Ag (110) surface. This is somewhat surprising since the (110) crystal face shows marked anisotropy in these two directions. Model calculations² which assume nearest-neighbor central forces predict the parallel rms displacement in $[001]$ direction to be the same as $\langle u_1^{\text{eff}} \rangle$ or even slightly larger, and to be markedly smaller than $\langle u_1^{\text{eff}} \rangle$ in the other parallel $[\bar{1}\bar{1}0]$ direction. Debye-Waller measurements on the Ni (110) surface⁹ seems to have confirmed this effect qualitatively, if not its magnitude. There may be several reasons for the lack of anisotropy in the parallel rms displacements in the Ag (110) surface: (a) 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 (b) The temperature dependence of dominant multiple-scattering events may mask the differences between the surface mean-displacement components. (c) 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 100–600°C⁴. Finally, (d) the accuracy of our experiment may be inadequate to detect small differences in the parallel rms displacements of surface atoms in silver.

The lack of any marked dependence of the parallel rms 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 rms 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 rms 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 fcc metals for which the effective mean displacements change most rapidly with electron energy along the $[\bar{1}\bar{1}\bar{1}]$ direction.^{6,7} However, silver appears to be different from other fcc metals in the fact that the surface rms displacement $\langle u_1^{\text{eff}} \rangle$ in the Ag (100) orientation is markedly larger than the (110) or (111) directions. For the other metals which were studied, $\langle u_1^{\text{eff}} \rangle$ 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 rms displacements and the change of the effective rms displacements with beam voltage. Calculations by Burton and Jura¹⁵ for several fcc 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 surfaces¹⁶ where, due to the formation of strong chemical bonds, the surface Debye-Waller factor changes markedly.

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¹⁵ J. J. Burton and G. Jura, *J. Phys. Chem.* **71**, 1829 (1967).

¹⁶ P. Estrup, in *The Structure and Chemistry of Solid Surfaces*, edited by G. A. Somorjai (John Wiley & Sons, Inc., New York, 1969), Chap. 19.