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Surface Lattice Dynamics of Silver. I. Low-Energy Electron Debye-Waller Factor*

EDWIN R. JONES
University of South Carolina, Columbia, South Carolina

AND

JAMES T. MCKINNEY
U. S. Steel Research Center, Monroeville, Pennsylvania

AND

MAURICE B. WEBB
University of Wisconsin, Madison, Wisconsin

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We have investigated the temperature dependence of the low-energy electron diffraction from the (111) surface of silver between 300 and 600°K using an apparatus containing a two-circle goniometer and provision for both visual display of the diffraction pattern and the more precise measurement of the diffracted current with a moveable Faraday cage. The penetration of the electrons is estimated from the energy dependence of the diffracted intensity and is shown to be described by an absorption coefficient which is approximately proportional to $E^{-1/2}$ for energies above 120 eV. Below 120 eV the penetration is a steeper function of energy. Measurements of the effective Debye temperature Θ' for various angles of incidence corroborate the functional dependence of the penetration of energy. From a knowledge of Θ' and the penetration, we estimate the mean square thermal displacements normal to the crystal surface as a function of depth. At the surface these displacements are 2.0 ± 0.2 times larger than in the bulk, and the amplitude approaches the bulk value nearly as e^{-n}, where n labels the plane. These results agree with recent model calculations. Measurements of the thermal displacements in other directions indicate that the excess amplitude is nearly isotropic, in disagreement with the model calculations.

INTRODUCTION

THERE has been considerable interest in the lattice dynamics of solid surfaces. Theoretical treatments for various models have been reported by several authors.[1–6] For example, Maradudin and Melngailis[4] have shown how to treat the dynamics of the surface by using the properties of the bulk crystal and representing the surface as an extended defect. They explicitly treat the case of a simple cubic lattice with central force nearest- and next-nearest-neighbor interactions of equal magnitude. The resulting mean square displacements $\langle u^2\rangle$ of the surface atoms are twice those of the interior atoms in a direction normal to the surface and 1.3 times greater in a direction parallel to the surface. This excess amplitude falls to its bulk value in a few interplanar spacings. Very similar results were obtained by Clark, Herman, and Wallis[5] who calculated $\langle u^2\rangle$ for atoms in the (100), (110), and (111) surfaces of a face centered-cubic (fcc) crystal with nearest-neighbor interactions.

There have also been several experimental investigations. Since the original experiments of Davisson and Germer,[7] a few observations of the temperature dependence of the low-energy electron diffraction have been made.[8–10] Recent experimental investigations have been made by Germer and MacRae,[11] and MacRae.[12] MacRae's experiments on Ni indicate that the mean square displacements of the atoms on the (110) surface are larger than for bulk atoms and that $\langle u^2\rangle[110] \approx \langle u^2\rangle[001] > \langle u^2\rangle[1\bar{1}0]$. There have also been two observations of the thermal diffuse scattering of low-energy electrons.[13,14] Finally there have been Mössbauer experiments with Fe^{57} absorbed on polycrystalline $\mathrm{Al_2O_3}$,[15] on W,[16] on Si,[17] and on Ag.[18]

We have made detailed measurements of the low-energy electron diffraction from the (111) surface of silver and its temperature dependence. In this paper we shall present results for the Debye-Waller factor as a

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function of electron energy and angle of incidence and an estimate of the penetration of the electrons into the crystal. From these results the mean square displacements of the atoms as a function of depth are derived. It is concluded that for atoms in the surface layer the component of $\langle u^2 \rangle$ normal to the surface is 2.0 ± 0.2 greater than for bulk atoms and that this excess amplitude falls nearly as e^{-n} where n indexes the planes parallel to the surface. These results are in good agreement with the model calculations. With considerably less precision the experiments indicate that the excess vibrational amplitude is nearly isotropic, in disagreement with theoretical expectations. However, this is perhaps due to nonideal experimental surfaces. It is also concluded that the penetration of the elastically scattered electrons into the silver crystal can be approximately described by a linear absorption coefficient given by $\mu = 1.4E^{-1/2}$ Å^{-1}, where E is the energy in electron volts.

We have also observed the thermal diffuse scattering of the electrons and measured its angular dependence, temperature dependence, and its integrated intensity. All these features agree well with those expected for the diffuse scattering of slightly penetrating radiation from a surface whose lattice dynamics are consistent with the above results. The work on the thermal diffuse scattering will be presented in a subsequent paper.

In this and the subsequent paper we shall interpret the diffraction only in terms of a pseudo-kinematical description. Each atom is thought to scatter independently an amplitude which depends only on its illumination by the incident field, and the scattering is assumed to be described by an atomic structure factor $f(\theta,E)$. This is equivalent to keeping only those terms in the Born approximation which represent single scatterings or multiple scatterings within the same atom. Such a description is known to be inadequate to account for all the features of the low-energy electron-diffraction data.[19,20] However, in our analysis we will examine features of the diffracted intensity only in the immediate vicinity of the diffraction maxima and usually only differences caused by temperature changes. Since these maxima come mainly from the terms included, it is hoped that the differences are insensitive to the multiple-scattering terms omitted. The consistency of the results on the lattice dynamics, derived from the data using this analysis, suggests that this is approximately true.

DEBYE-WALLER FACTOR FOR LOW-ENERGY ELECTRONS

We first consider the modifications of the Debye-Waller effect to be expected for slightly penetrating radiation. For penetrating radiation incident on a lattice of independent oscillators, the time-averaged scattered intensity is given by[21]

$$\langle I(\mathbf{S})\rangle = |f_0|^2 e^{-2M} \sum_i \sum_j e^{i\mathbf{S}\cdot(\mathbf{r}_i-\mathbf{r}_j)}, \tag{1}$$

where

$$M = 8\pi^2 \langle u^2 \rangle \sin^2\phi/\lambda^2, \tag{2}$$

and where f_0 is the atomic structure factor, $\mathbf{S}$ is the diffraction vector $(\mathbf{k}-\mathbf{k}_0)$, $\langle u^2 \rangle$ is the mean square displacement of the atoms from their equilibrium position parallel to $\mathbf{S}$, ϕ is the Bragg angle, λ is the wavelength of the scattered radiation, and $\mathbf{r}_i$ is the equilibrium position of the ith atom.

For a Debye spectrum in the high-temperature limit, $\langle u^2 \rangle = 3\hbar^2 T/mk\Theta_\infty^2$, where Θ_∞ is the Debye temperature of the bulk crystal, k is the Boltzmann constant, and m is the atomic mass. Thus $2M$ is directly proportional to T and therefore diffracted intensity decreases exponentially with increasing temperature, but the diffraction maxima remain sharp. The restriction to independent oscillators does not affect the Debye-Waller factor but of course must be dropped in the discussion of the thermal diffuse scattering.

In the case of slightly penetrating radiation, we write the time average of the diffracted intensity as

$$\langle I(\mathbf{S})\rangle = |f_0|^2 \sum_i \sum_j a_i a_j e^{i\mathbf{S}\cdot(\mathbf{r}_i-\mathbf{r}_j)} \langle e^{i\mathbf{S}\cdot(\mathbf{u}_i-\mathbf{u}_j)}\rangle, \tag{3}$$

where $f_0 a_i$ is the amplitude scattered by the ith atom. We again temporarily assume that the atoms are independent oscillators whose mean square vibrational amplitudes as a function of depth in the crystal are given by

$$\langle u_n^2 \rangle = \langle u_\infty^2 \rangle (1 + AF_n), \tag{4}$$

where $\langle u_n^2 \rangle$ is the projection along $\mathbf{S}$ of the mean square amplitude of the atoms in the nth plane, A is the excess amplitude of the surface atoms, and F_n is a function telling how rapidly the excess amplitude falls with distance into the crystal. $F_0 \equiv 1$.

We also suppose that the ratio of the electron amplitude scattered by atoms in the $(n+1)$st and the nth atomic planes is given by $\alpha = a_{n+1}/a_n$ so that $a_i = \alpha^n$ when the ith atom is in the nth plane.

With these assumptions, the time-averaged intensity of Eq. (3) can be evaluated for values of $\mathbf{S}$ satisfying the three Laue equations, giving

$$\langle I(\mathbf{S})\rangle \propto \left[e^{-(1/2)|\mathbf{S}|^2\langle u_\infty^2\rangle} \sum_{n=0}^{\infty} \alpha^n e^{-(1/2)|\mathbf{S}|^2\langle u_\infty^2\rangle AF_n} \right]^2 \tag{5}$$

and

$$\frac{d \ln\langle I(\mathbf{S})\rangle}{dT} = -2b\left[1 + \left(A \sum_{n=0}^{\infty} \alpha^n F_n e^{-bTAF_n} \Big/ \sum_{n=0}^{\infty} \alpha^n e^{-bTAF_n}\right)\right], \tag{6}$$

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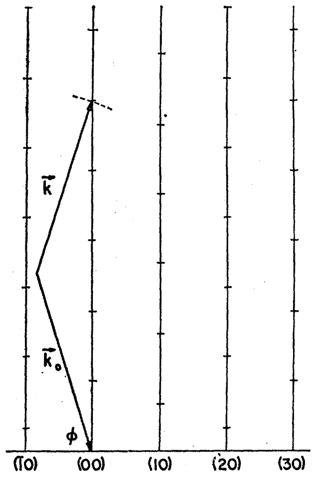

FIG. 1. Reciprocal space for two dimensional lattice. $\mathbf{k}_0$ and $\mathbf{k}$ are the wave vectors of the incident and scattered beams. The dashed line indicates the motion of the detector. ϕ is the grazing angle of incidence.

where

$$b=6h^2\sin^2\phi/mk\Theta_\infty{}^2\lambda^2. \quad (7)$$

The slope of $\ln I(\mathbf{S})$ versus T is no longer constant, but for reasonable values of the parameters the slope changes by only $\cong 1\%$ over a range of 200 or 300°K. Thus from the slope of $\ln I(\mathbf{S})$ versus T an effective Debye temperature Θ' may be determined. Θ' determined experimentally will be a function of the energy of the electrons through the energy dependence of α. Lower energy electrons, which sample the outer layers more strongly, will give lower Θ''s. Experimentally, then, one must determine the α's, measure Θ' as a function of electron energy, and choose values of A and functions F_n to fit the resulting data.

EXPERIMENTAL

A low-energy electron-diffraction apparatus has been constructed which provides for both the visual display of the diffraction pattern and for direct measurement of the scattered intensity with a moveable Faraday collector. The crystal was mounted on a two-circle goniometer with axes both normal to and in the plane of the crystal surface. Racks to rotate the goniometer and collector entered the vacuum system through flexible metal bellows. A standard cathode-ray gun designed for operation at low voltages provided an incident beam focused on the crystal to a spot about 1 mm in diameter with an estimated divergence of less than 1°. The diffraction could be observed visually with a fluorescent screen in the manner described by Scheibner, Germer, and Hartman[22] in order to facilitate identification of the diffracted beams and to orient the crystal. All quantitative measurements of the scattering to be reported here were made with the Faraday collector which could be rotated independently about the goniometer axis in the plane of the crystal. The scattering angle could be measured absolutely to approximately 1°, but changes in this angle could be measured to (1/40)°. The entrance slit of the collector was 0.010 in.×0.040 in. and subtended an angle of 0.28° in colatitude at the center of the goniometer. No careful investigation of the electron optics has been made and no detailed information about the physical width of the narrowest diffraction maxima was obtained. However, the narrowest diffraction peaks observed had a full width at half-maximum of 1.0°, which is comparable with the estimated instrumental width. The Faraday collector was made of three concentric cylinders in order to select only the nearly elastically scattered electrons and to guard against small leakage currents over the surfaces of various insulators.

The sample was mounted on a tantalum can and heated from underneath by radiation from a filament. The temperature was measured with a Pt-PtRh thermocouple attached to one of the tabs holding the crystal. Auxiliary experiments indicate the resulting errors were less than 1°C.

The glass vacuum system was pumped with a 2-in. orbitron.[23,24] After bakeout the indicated pressure was essentially the x-ray limit of the vacuum gauge, but diffraction results imply partial pressures of gases adsorbable on silver were on the order of 10^{-12} or 10^{-13} Torr.

The silver single crystals were grown from 99.999% pure silver by zone melting and cut to reveal faces parallel to the (111) surface to within ½°. Damage was removed by successive lapping and mechanical polishing. The final mechanical polish was on cloth containing 0.05 μ alumina. The crystals were then chemically polished by swabbing with a solution of 100 ml saturated chromic acid and 5 ml of 5% HCl.[25] To assure a damage-free surface and to correct for imperfect alignment, the crystals were etched to reveal (111) facets as described by Farnsworth.[26]

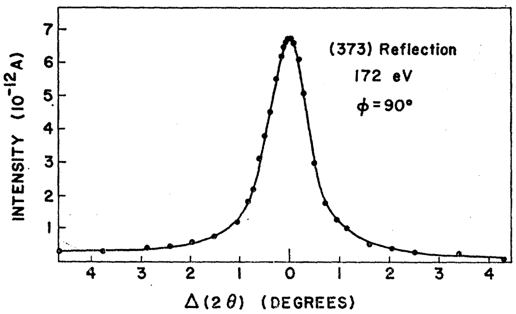

FIG. 2. Profile of the diffracted beam for the detector crossing the (20) reciprocal-lattice rod at the position of the (373) reciprocal-lattice point.

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The crystal was cleaned by heating several times in the vacuum system to temperatures between 700 and 800°C at pressures less than 2×10^{-9} Torr for periods of 10–15 min. Sometimes, before the cleaning was completed, weak fractional-order diffraction spots could be seen which indicated surface structures with unit cells greater than that of the substrate. These structures, presumably resulting from gases adsorbed on the surface, were removed by continued heating. After several weeks without further cleaning the additional spots were again faintly visible, and heating again removed them. After the cleaning was completed no evidence for the fractional order reflections was seen either on the fluorescent screen or with the Faraday collector. For the cleaned crystal all of the diffraction peaks expected from a silver surface were observed and no others. The diffraction was stable for more than a week and there were no observable changes in the diffraction after subsequent heat treatments to 800°C. We take these observations as evidence that the surfaces were atomically clean in agreement with earlier work by Farnsworth.[26]

In these experiments the detector cut across the rods in reciprocal space as shown in Fig. 1. The angle between the path of the detector and the rod depends on the tilt of the crystal and the scattering angle and for most measurements was in the vicinity of 70°. The profile of a typical diffraction peak is shown in Fig. 2. The shape of the central peak is nearly Lorentzian. The broad wings extend far into the Brillouin zone and are associated with the thermal diffuse scattering.

On some early crystals the diffraction peaks were observed to broaden reversibly with temperature, due to some thermal disorder in the crystal surface. However, such broadening of the diffracted beam was not seen with later crystals on which more care had been taken with surface preparation. The results to be presented are from these better surfaces.

ELECTRON PENETRATION

The penetration into the crystal of the elastically scattered electrons will first be estimated from measurements of the modulation of the diffracted intensity along rods in reciprocal space. Because of the well-known difficulties in understanding all features of these data, this is a questionable procedure. In a next section an independent check of at least the energy dependence of the penetration is available from the temperature measurements.

The data were obtained by measuring diffraction peaks such as those shown in Fig. 2 at intervals of 2.5 eV or less for a range of energies between 20 and 320 eV. Such data were taken for several reciprocal-lattice rods and for several angles of incidence. A plot of the maximum of the peaks versus energy for data on the (00) rod and an angle of incidence of 68° is shown in Fig. 3. Repetition in entirely independent experiments gives agreement within experimental uncertainties for the positions of the maxima in such data. However, the relative magnitudes of various features vary somewhat. This variation may be due to small uncertainties in the angles of the experiment and small changes in the position of the incident beam on the crystal. However, there are generally prominent maxima at the energies predicted by the third Laue equation with an approximately constant inner potential of about 15 V. These maxima behave correctly with changes in the angle of incidence. Other maxima satisfy the third Laue condition with no inner potential correction and are presumably due to steps on the surface.

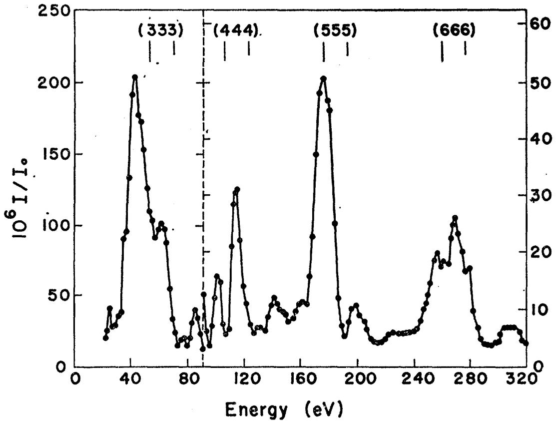

FIG. 3. Energy dependence of the diffracted intensity measured along the (00) reciprocal-lattice rod of the (111) surface of silver. Angle of incidence = 68°; $T=299$°K. The short dashes at the top indicate the energy of three-dimensional reflections with no inner potential. The long dashes indicate the energies for the three-dimensional reflections assuming a constant inner potential of 15 V.

Clearly there is more structure in the data than can be explained by a simple pseudo-kinematical description. However we shall assume that in the immediate vicinity of the maxima due to the residual third Laue equation, the energy dependence is dominated by interference between wavelets scattered by successive atomic planes.

We proceed in a manner similar to that of Lander and Morrison.[19] The total scattered amplitude, $a(\lambda)$, along the (00) reciprocal-lattice rod will be given by

$$a(\lambda)=a_0\sum_{n=0}^{\infty}\alpha^n e^{in4\pi d\sin\phi/\lambda}=a_0\sum_{n=0}^{\infty}a^n e^{in\delta}, \qquad (8)$$

where a_0 is the amplitude scattered by the outermost plane, $\alpha=a_{n+1}/a_n$ is the ratio of the amplitudes scattered by atoms in the $(n+1)$st and nth planes, d is the interplanar spacing, ϕ is the angle of incidence, λ is the wavelength within the crystal, and δ is the phase shift between wavelets scattered by successive planes. The intensity is then

$$I=I_0|1/(1-\alpha e^{i\delta})|^2, \qquad (9)$$

and the phase shift at which the intensity falls for

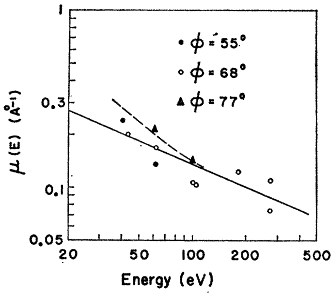

FIG. 4. Linear absorption coefficient versus electron energy. The solid line is a least-squares fit to the data. The dashed line is discussed later in the text.

example to $\frac{3}{4}$ of its maximum value will be given by

$$I(\delta=\delta_{3/4})/I(\delta=m\pi)=\tfrac{3}{4}=|1-\alpha|^2/|1-\alpha e^{i\delta_{3/4}}|^2, \quad (10)$$

which when solved for $\delta_{3/4}$ gives

$$\cos\delta_{3/4}=-(1/6\alpha)(1-8\alpha+\alpha^2). \quad (11)$$

In terms of the energies E_1 and E_2 at which the intensity has fallen to $\frac{3}{4}$ of its maximum value on either side of the peak

$$\delta_{3/4}\cong 1.21 \sin\phi[E_1^{1/2}-E_2^{1/2}]. \quad (12)$$

Thus from experimental values of E_1 and E_2, values of α can be determined from Eq. (11). This has been done for a large number of maxima for data such as that shown in Fig. 3. Only those maxima clearly associated with the third Laue equation and seemingly well separated from other structure were used to determine values of α. α is a function of the angle of incidence as well as the energy and thus the results are difficult to summarize systematically. We present the results below in a different form. However, for $\phi=68°$, $\alpha=0.38$ at 50 eV and $\alpha=0.63$ at 271 eV.

We have neglected effects of the thermal vibrations on α. Such effects, to be determined in a later section, should be included in Eq. (8) and the whole procedure should be iterated. This has been done for one case [the maximum in the vicinity of the (555) peak] and the result changes by less than the experimental uncertainty.

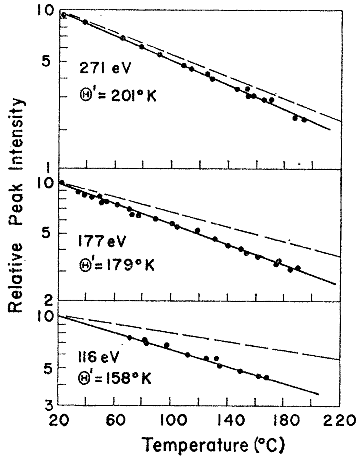

FIG. 5. Diffracted intensity versus temperature in the vicinity of several three-dimensional maxima on the (00) reciprocal-lattice rod. The dashed lines indicate the temperature dependence calculated from the bulk properties of silver. Θ′ is the effective Debye temperature calculated from the solid lines.

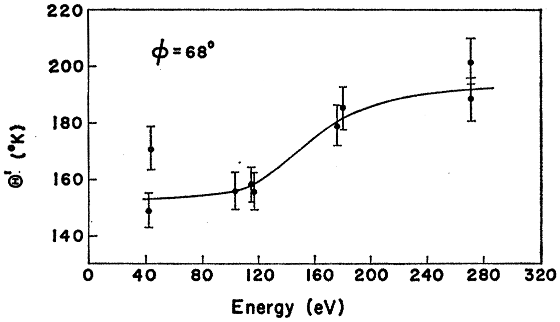

FIG. 6. Measured effective Debye temperature versus energy. Angle of incidence = 68°.

If the penetration of the electrons into the crystal depends only on their path length in the crystal and not, for example, on the number of planes crossed or on the direction of the beam, then one can define a linear absorption coefficient μ such that

$$a_{n+1}/a_n=\alpha=e^{-2\mu d/\sin\phi}, \quad (13)$$

where μ is assumed to depend only on the energy. Values of μ determined from Eq. (13) for various reflections and angles of incidence are plotted in Fig. 4 as a function of energy. The derived values of μ are quite sensitive to the widths of the intensity maxima along the reciprocal-lattice rod, and thus there is considerable scatter in the results. However, there is no systematic variation of μ with the angle of incidence, lending some support to the assumptions leading to Eq. (13). A least-squares fit of $\mu\propto E^{-\gamma}$ gives $\gamma=0.43\pm0.06$ or nearly $\mu\propto E^{-1/2}$ as might be expected from the total inelastic cross section for slow particles from a local potential.[27] Certainly the estimated penetration is of the correct order of magnitude. It is comparable with estimates for other materials[19] and with Farnsworth's estimate for silver obtained from experiments using evaporated films of silver.[26] It is clear that the energy dependence of the penetration is more uncertain, but temperature experiments, to be discussed below, will give additional confidence that the estimated dependence is approximately correct.

TEMPERATURE DEPENDENCE

Diffraction profiles such as the one shown in Fig. 2 were taken across the (00) reciprocal-lattice rod at closely spaced temperatures between 20 and 300°C. These measurements were made at energies satisfying the third Laue condition. This provides a maximum intensity and minimizes the effect of small variations which might occur in the orientation of the crystal as the temperature changes. Furthermore, it is for these values of S that Eq. (5) was derived. The observed shape and width of the diffraction peaks did not change

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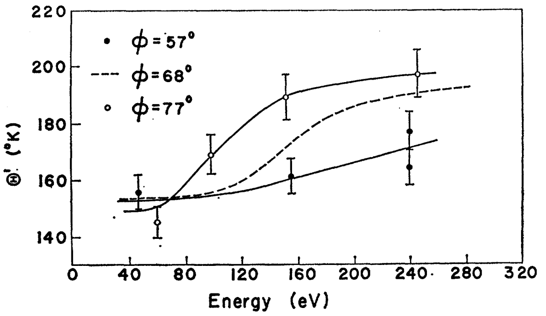

FIG. 7. Measured effective Debye temperatures for angles of incidence of 57° and 77°. Dashed line is from Fig. 6, for an angle of incidence of 68°.

with temperature in the experiments to be reported. The intensities were reversible with temperature and in most cases were measured with both increasing and decreasing temperature. The current in the incident beam was measured and held constant throughout each experiment. There were small changes in the angular position of the maximum of the diffraction peak with changes in temperature, which were presumably due to changes in the orientation caused by changing the temperature of the goniometer. These changes were corrected for by small changes of the crystal orientation to keep the scattering angle for peak intensity constant. This procedure considerably reduced the scatter in the experimentally measured intensities.

Representative data are shown in Fig. 5. Maxima of the diffraction peaks versus temperature are plotted for several energies at an angle of incidence of 68°. The solid lines on the semilog plots were determined by a least-squares fit with probable uncertainties of less than 2%. The dotted lines give the results expected from the bulk properties of silver. From the slopes of the experimental data, effective Debye temperatures Θ' were determined from

$$I(T) \propto e^{-2M},$$

where

$$M = \frac{6h^2T}{mk\Theta'^2}\,\frac{\sin^2\phi}{\lambda^2}.$$

Uncertainties in slope, energy, and the angle of incidence give an uncertainty in the measured Θ''s of about 4%. Completely independent measurements of Θ' at the same energy and angle of incidence agree to within this uncertainty.

In Fig. 6, Θ' is plotted as a function of the electron energy for reflections along the (00) rod and an angle of incidence of 68°. It is evident that higher energy electrons penetrate more deeply into the crystal and sample thermal vibrations approaching those of the bulk material, while lower energy electrons give Θ''s appropriate to the excess vibrational amplitudes of the surface layers. Two conclusions may be drawn from this plot even without detailed analysis. First, the measured effective Debye temperature cannot be lower than that corresponding to the plane of atoms, presumably the outermost, with the largest vibrational amplitude. Therefore, since values of Θ' as small as 155°K are observed, the atoms in the surface plane must have mean square amplitudes normal to the surface at least 1.8 times greater than the bulk atoms. Secondly, since Θ' approaches the bulk value for 280 eV electrons, the vibrational amplitude must fall nearly to the bulk value in depths comparable with the penetration of these electrons.

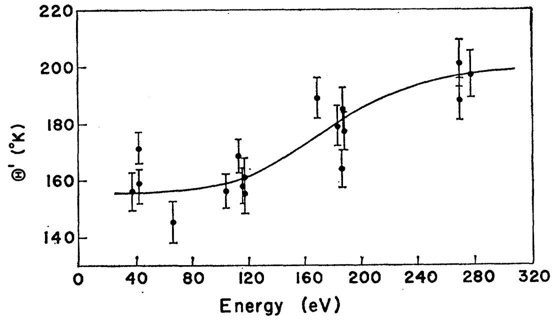

FIG. 8. Measured effective Debye temperatures versus energy for several angles of incidence. The data points have been shifted in energy according to Eq. (14) with $\phi_1=68°$ and with $\mu(E)$ taken from the solid line of Fig. 4.

Before considering these data further, we shall give similar results for various angles of incidence in order to obtain an additional estimate of the penetration of the elastically scattered electrons. In Fig. 7, Θ' is plotted versus energy for three angles of incidence for reflections on the (00) rod. As would be expected, beams farther from normal incidence sample the deeper planes less strongly because of their longer paths in the

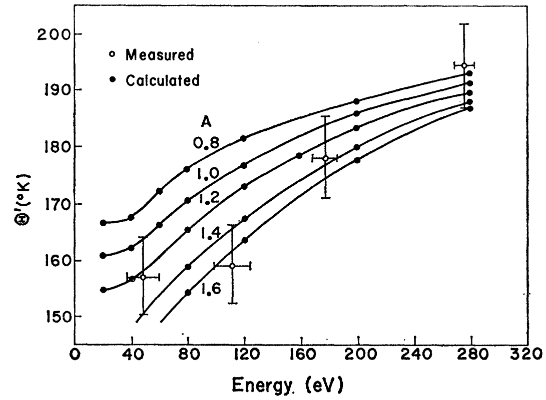

FIG. 9. Calculated effective Debye temperatures versus energy. The solid lines connect points calculated from Eq. (5) using $\mu(E)$ from the straight line of Fig. 4, F_n from Ref. 5, and various values of A. The open circles represent averages of Θ' measured within the energy range indicated by the horizontal error bars. The vertical error bars indicate the scatter plus the uncertainties of the measured values of Θ' within this energy range.

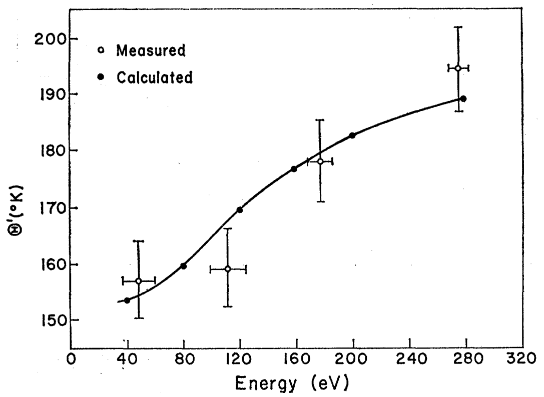

FIG. 10. Calculated effective Debye temperatures versus energy. The full circles are calculated from Eq. (5) using $A=1.2$, F_n from Ref. 5, and $\mu(E)$ from the dashed curve of Fig. 4.

crystal to reach a given depth. Therefore, they give lower effective Debye temperatures. Values of Θ' measured at different angles of incidence should not be compared at the same energy but rather should agree at energies such that the relative amplitude scattered by a given plane is the same. Thus, according to the assumptions leading to Eq. (13), values of Θ' should be the same at energies such that

$$\mu_1/\sin\phi_1=\mu_2/\sin\phi_2. \tag{14}$$

In Fig. 8 we replot the data of Figs. 6 and 7 after shifting the points for $\phi_2=77°$ and $57°$ to voltages such that Eq. (14) is satisfied with ϕ_1 equal to 68°. We have used the relation between μ and E plotted as the straight line in Fig. 4. We see that in this sense the results for various angles of incidence agree well. Similar comparisons using $\mu=E^{-\gamma}$ for other values of γ give comparable fits for $\frac{1}{4}\lesssim\gamma\lesssim\frac{1}{2}$, but unacceptable fits for γ outside of this range. Thus in the region between 100 and 300 eV, where Θ' is a rapid function of E, these results give an independent estimate of the energy dependence of the penetration of the elastically scattered electrons.

We now return to the energy dependence of the observed Θ' and attempt to find a value of A and a function F_n which best fit our data. To do this, the sum in Eq. (5) is computed using various functions F_n and values of A. Values of $|\mathbf{S}|$ are taken from the data,[28] the α's are calculated from the μ's of Fig. 4, and $\langle u_\infty^2\rangle$ is taken from x-ray data.[29] Guided by model calculations, we are interested in A's near 1.0 and F_n's similar e^{-n}.

Figure 9 shows Θ' versus E calculated from Eq. (5) using the function F_n calculated by Clark, Herman, and Wallis,[5] and various values of A. The major discrepancy is that the inflection points for the calculated curves occur at considerably lower energies than is observed in the experimental data. This discrepancy is not lessened by other reasonable choices of F_n. The fact that Θ' is slowly varying with energy below 100 eV suggests that, for these energies, the electrons penetrate less than is indicated by the straight line of Fig. 4. To check this suggestion, we have computed $d\log\langle I\rangle/dT$ for several rather arbitrary choices of $\mu(E)$ which fall within the scatter of the points in Fig. 4. One such choice is shown by the dashed line in Fig. 4. Using this choice of $\mu(E)$ and F_n from Clark, Herman, and Wallis,[5] the best fit is given by $A=1.2$ and is plotted in Fig. 10. We have found no reasonable choice of $\mu(E)$ and F_n which show a nearly flat region at low energy and fit the data with A's of 1.4 or 1.6. In fact, somewhat smaller values of A and a more pronounced plateau would be obtained if $\mu(E)$ were even larger than we have chosen here. However, no such $\mu(E)$ lies within the scatter of the data of Fig. 4. Thus we conclude that A must be between 1.2 and the lower limit of 0.8.

The calculated results for various functions F_n and $A=1.2$ are presented in Fig. 11. Equally good fits occur for $F_n=e^{-n}$ or for the F_n from the results of the model calculations.[4,5] Functions which cut off more slowly than e^{-n} do not fit the data. It might appear that functions which fall even more sharply than e^{-n} could fit the data with larger A's but one cannot reproduce the plateau of Θ' versus E at low energy for any reasonable $\mu(E)$.

$\langle u^2\rangle$ IN OTHER DIRECTIONS

We also examined $\langle u^2\rangle$ in directions other than normal to the surface of the crystal. The data are given in Table I. To compare the values of Θ' for various reflections with those obtained along the (00) reciprocal-lattice rod, the effects of penetration were treated by the method used above for comparing values of Θ' measured at different tilts. These values of Θ' are shown in Fig. 8 after adjusting their energies for comparison with the (00) results at $\phi=68°$. For **S** and thus $\langle u^2\rangle$ inclined up to 39° from the surface normal, Θ''s are the same as for the (00) reflection to within our experimental error.

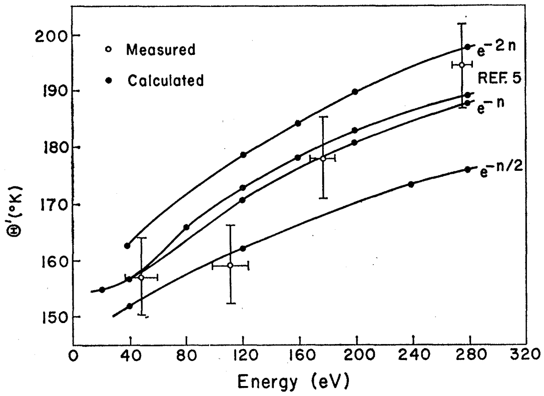

FIG. 11. Calculated effective Debye temperatures versus energy. The full circles are calculated from Eq. (5) using $\mu(E)$ from the dashed line of Fig. 4, $A=1.2$ and various F_n's.

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[28] In determining $|\mathbf{S}|$ we have used the wavelength calculated for zero inner potential. Calculations made with an inner potential of 15 V gave values of Θ' which agreed to within $\frac{1}{2}\%$.

[29] F. H. Herbstein, Advan. Phys. 10, 313 (1962).

TABLE I. Effective Debye temperatures for non-(00) reflections.

Peak (*hkl*)	Beam energy (eV)	Effective Debye temperature Θ' (°K)	ϕ_1 (deg)	ϕ_2 (deg)
(151)	72	154	75	25
(242)	46	162	88	39
(353)	93	150	80	46
(262)	113	154	80	40
(282)	175	174	76	35
(282)	177	152	75	$32\frac{1}{2}$
(373)	172	177	90	41
(464)	180	164	76	55

For vibrations parallel and perpendicular to the surface which are independent or coupled with a 90° phase shift, we may write

$$\langle u^2(\omega)\rangle = \langle u_\perp^2\rangle \cos^2\omega + \langle u_\parallel^2\rangle \sin^2\omega\,, \tag{15}$$

where ω is measured from the surface normal, and $\langle u_\parallel^2\rangle$ and $\langle u_\perp^2\rangle$ are the parallel and perpendicular components of the mean square amplitude. Thus, from measurements of $\langle u^2(\omega)\rangle$ we can investigate $\langle u_\parallel^2\rangle$. In our experiments, we are limited to values of ω less than 40°, and so $\langle u^2(\omega)\rangle$ is dominated by $\langle u_\perp^2\rangle$. Therefore the uncertainties in the evaluation of $\langle u_\parallel^2\rangle$ are large. Errors propagate in Eq. (15) to give an uncertainty of 24% in $\langle u_\parallel^2\rangle$. We conclude that within this uncertainty $\langle u_\parallel^2\rangle = \langle u_\perp^2\rangle$ and the excess surface amplitude is isotropic.

COMPARISON WITH MODEL CALCULATIONS

There are three points at which comparison of our results with the theoretical calculations may be made. First, we have determined that the surface atoms have a component of their mean square displacement perpendicular to the surface which is between 1.8 and 2.2 times that for atoms in the bulk. Clark, Herman, and Wallis[5] calculated the corresponding quantity for an fcc lattice with nearest-neighbor central forces and obtained a value of 2.02. Maradudin and Melngailis[4] treated an isotropic simple cubic lattice in which it is assumed that the force constants for the nearest and next-nearest neighbors are equal. They also obtained a value of very nearly 2.0. Thus, our value agrees with the model calculations within the experimental uncertainty of approximately 10%.

Second, we find that the excess perpendicular surface amplitude falls rapidly to the bulk in agreement with the model calculation and goes approximately as e^{-n}.

Third, we find that the mean square displacements parallel and perpendicular to the surface are equal to within 25%. However, all the calculations suggest that $\langle u_\perp^2\rangle$ should be greater than $\langle u_\parallel^2\rangle$ by a factor of 1.5 for close-packed surfaces. Thus, our result of 1 ± 0.25 disagrees with these calculations. It is true that these model calculations were not done specifically for silver and that the ratio of sound velocities for the model crystals and for silver are quite different. Therefore the discrepancy is perhaps not surprising and a more appropriate model calculation might agree with the experimental result. A possible alternative explanation lies in the fact that the calculations deal with atomically flat surfaces. The actual surface undoubtedly contains many steps and perhaps other imperfections. Such a nonideal surface will contain atoms with neighbors missing in the direction parallel to the nominal surface. In the crude broken-bond arguments such atoms would have larger amplitudes parallel to the surface. Calculation of the normal modes of vibration of a crystal with such a nonideal surface seems impossibly complicated, but would lead to larger amplitudes in directions parallel to the surface. The continuous area of facets cannot necessarily be determined by the breadth of the reflections since radiation scattered from several surface patches at the same level will still interfere as if from a continuous patch.

The expected anisotropy in $\langle u^2\rangle$ which is not evident in our experiments on the (111) surface of silver has been indicated in some other experiments, notably in the work of A. U. MacRae[12] on Ni.