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Oscillatory relaxation of the Ag(110) surface

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The relaxation of the Ag(110) surface was studied by high-energy ion scattering. We find the first-layer spacing contracted by $(7.8\pm2.5)\%$ and the second-layer spacing increased by $(4.3\pm2.5)\%$. The sensitivity of these results to assumptions of surface vibrations is explored. It is shown that the nearest-neighbor spacing at the surface (i.e., the spacing between the first and third layers) is contracted by $(3.5\pm0.5)\%$, and this result is almost independent of the surface Debye temperature. The results are consistent with the body of data indicating large, multilayer relaxation in (110)fcc surfaces.

INTRODUCTION

Surface relaxation, a layer spacing at a solid surface difference from that in the bulk, is one possible surface rearrangement. Oscillatory relaxation, an alternating change in sign of the relaxation in the first few layers, was first predicted by Landman *et al.*,[1,2] and the existence of this phenomenon has been explored by low-energy electron diffraction (LEED) for bcc V(100),[3] fcc Al(110),[4] and Cu(110).[5,6] In this last case oscillatory relaxation was confirmed by both low-energy electron diffraction and high-energy ion scattering.[6] In this paper, we report on the multilayer relaxation of the unreconstructed Ag(110) surface measured by ion scattering.[7] We have found the change of the first-layer spacing $\Delta_{12}=-(7.8\pm2.5)\%$, and that of the second-layer spacing $\Delta_{23}=(4.3\pm2.5)\%$ of the bulk value, using a surface Debye temperature Θ_s of 149 K. (A negative sign denotes a contraction relative to the bulk spacing.) Our analysis shows that the value of the individual layer relaxations is dependent on the value of Θ_s but the sum $\Delta_{12}+\Delta_{23}=-(3.5\pm0.5)\%$ is almost independent of Θ_s.

Earlier LEED results for Ag(110) deduced a contraction of the first-layer spacing only. Four different groups reported Δ_{12} to be -7% (Ref. 8), -8% (Ref. 9), -10% (Ref. 10), and -6.6% (Ref. 11) by an analysis of the diffracted intensity as a function of electron energy. In a new analysis, however, Davis and Noonan[12] reported a two-layer relaxation of the Ag(110) of $\Delta_{12}=-5.7\%$ and $\Delta_{23}=2.2\%$. In view of the variation of the LEED analyses it was deemed appropriate to employ the ion-scattering technique.

EXPERIMENT

The ion-scattering experiments were performed in an ultrahigh vacuum (UHV) system equipped with LEED and Auger apparatus to characterize the surface cleanliness and order. The UHV system is directly connected to a Van de Graaff accelerator for ion-scattering—channeling analysis. The principles of ion scattering for surface studies are explained elsewhere.[13]

It is known that the characteristics of the Ag(110) surface are sensitive to the history of the sample preparation.[14] Four different single crystals of the Ag(110) were used for the present experiment with four different methods of initial preparation; a mechanical polishing, a mechanical polishing and chemical etching, an electropolishing, and an electropolishing and chemical etching. The surface peak and minimum yield, which indicate the quality of crystallinity, were the smallest for the sample finished by electropolishing and chemical etching, while other samples, prepared in different ways, had some strain near the surface. After polishing and etching, the Ag(110) sample was cleaned *in situ* by sputtering and annealing. many cycles a sharp (1×1) LEED pattern was observed and there was no trace of impurities by Auger analysis or ion scattering.

Initially the energy dependence of the surface peak was measured along the [110] normal and [101] non-normal directions of the surface. Normal measurements are sensitive to displacements in the surface plane while an off-normal measurement is sensitive to surface relaxation, since the displacement is projected out from the aligned crystal string. For displacements greater than the shadow-cone radius (0.1—0.3 Å) relaxation is observed by an increase in the measured (off-normal) surface peak over that expected for a bulklike surface. If the displacement is within the shadow cone at a certain energy, it can be measured by a surface-peak "angular scan" about a non-normal axis in an azimuth corresponding to a major plane.[7] For multilayer relaxation, the surface-peak angular scan can be measured along several non-normal directions. In this experiment, we measured the energy dependences and angular scans along the normal [110], and two non-normal directions [101] and [100].

RESULTS AND DISCUSSION

The energy dependence of surface peak was measured along the [110] direction of the Ag(110) at room temperature [Fig. 1(a)]. The data are for four different samples, all finished by electropolishing or chemical etching, and the solid line is the result of numerical simulations[15] assuming a surface with bulklike termination and a bulk vibration amplitude, $\Theta_B=215$ K, with a two-body correla-

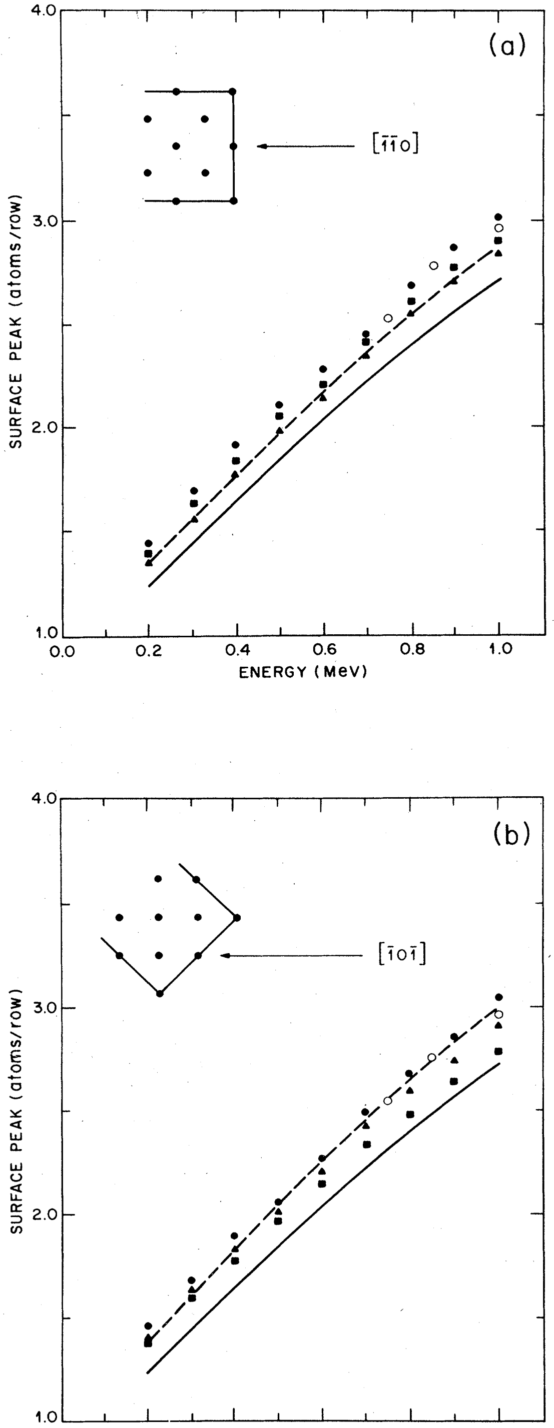

FIG. 1. Energy dependence of the surface peak measured along the (a) [011] and (b) [101] directions of four different Ag(110) samples. Solid circles correspond to a sample with only chemical etching; all other samples were prepared by electropolishing and chemical etching. The solid lines correspond to the calculated surface-peak values for a bulklike structure while the dashed line includes enhanced-surface vibration. For (b) the dashed line also includes the optimum relaxation.

tion coefficient of 0.38. The dotted line indicates the calculated surface peak including correlation, and an enhanced isotropic surface vibration in the first layer ($\Theta_s = 149$ K).

Figure 1(b) shows the energy dependence of the surface peak along the [101] direction. Although data points are somewhat scattered, they are within the quoted absolute error, ±5%. The spread in data points is a true measure of the degree of reproducibility, from sample to sample, in these Ag surface-peak measurements. Other surfaces, such as Si, have yielded closer reproducibility for different samples. All of the Ag samples measured showed the same relaxation effects.

The solid line is the calculated surface peak with bulklike termination as in Fig. 1(a); the dotted line indicates the surface peak with the enhanced vibration and correlation. The relatively good agreement between these absolute values of the measured surface peak and the calculation is another indication [in addition to the (1×1) LEED pattern] that Ag (110) is an unreconstructed surface. In this context the term reconstructed refers to displacements in the plane of the surface. A variety of clean reconstructed surfaces [i.e., those showing other than a (1×1) LEED pattern] yield surface peaks far in excess of the calculated value.[16] For example, if all atoms with the first layer are displaced laterally the measured value would exceed the calculated value (solid line) by 1.0 atom/row in Fig. 1(b). The small difference between experimental and calculation is most naturally explained by a change in the surface Debye temperature and not a reconstruction. The effect of the surface Debye temperature in extracting the relaxation will be discussed in detail in the latter part of this paper.

Quantitative information on double-layer relaxation is precisely obtained from angular scans, which are sensitive to small displacements, close to 10^{-2} Å. Relaxation is indicated through an asymmetric scan of the surface peak about the bulk channeling direction. Angular scans of the surface peak were performed in the (111) plane about the [101] direction. The results are shown in Fig. 2 for the case of 400-keV He^+ incident energy with the sample at room temperature for two different scattering geometries; with a detector at a forward angle (~40°) and in a back angle (~160°). The scan is clearly asymmetric about the $\theta = 0°$ line which is determined from scattering from the bulk. We have tried to fit the data with single-layer relaxations, such as $\Delta_{12} = -1\%$, -2%, -3%, -4%, and -5% [Fig. 2(a)]. These calculated curves, which use bulklike vibrations, do not show good agreement with the data. Other single-layer-relaxation models (-7%, -8%, and -10%) are also in poor agreement with the data.

If we vary the vibration amplitude of the surface atoms (corresponding to $\Theta_s = 60$ K to $\Theta_s = 215$ K) maintaining single-layer relaxation, the overall fit of the calculated curve still shows poor agreement with the data. The next simplest model is a double-layer relaxation, where the surface Debye temperature is also a variable. Figure 2(b) shows model calculations for double-layer and single-layer relaxation using $\Theta_s = 149$ K in both cases.

We have performed the R-factor analysis to obtain the "best-fit" values of Δ_{12} and Δ_{23}. The method is similar to

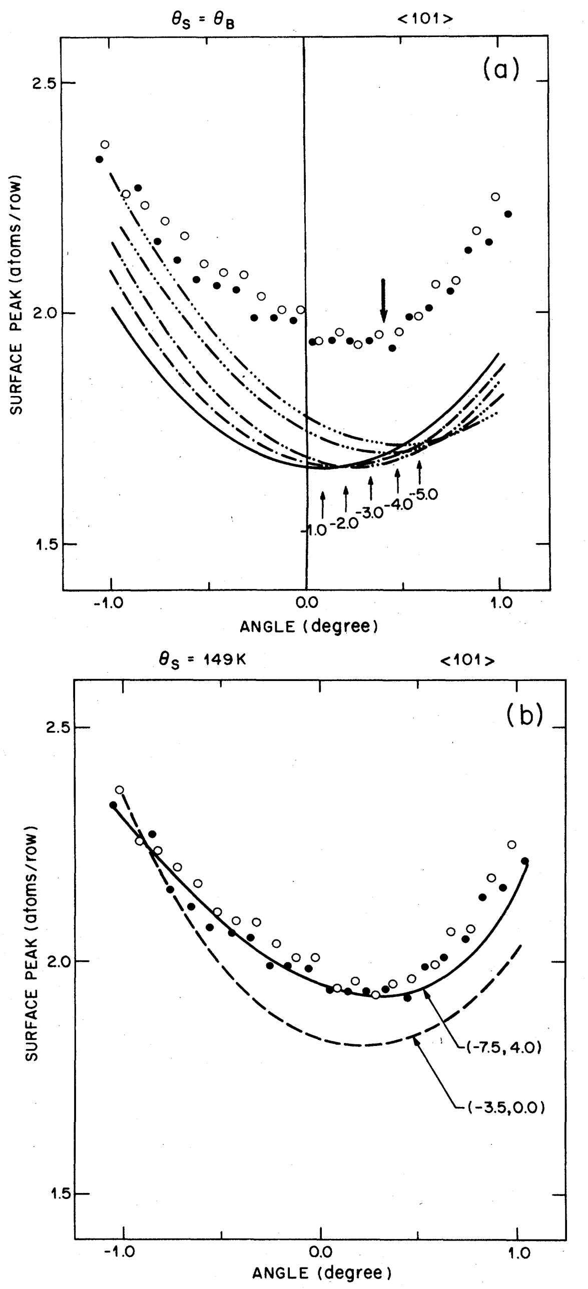

FIG. 2. Angular scan of the surface peak measured near the [101] direction in the (111) plane. (a) The calculated curves assume single-layer relaxations of -5%, -4%, -3%, -2%, and -1%. (b) Comparison of the measured angular scan to calculation for two-layer relaxation (-7.5%, $+4.0\%$) and single-layer relaxation.

that described in Ref. 6, but without the arbitrary normalization constant which scales (over a narrow interval) the magnitude of the surface peak. In our analysis

$$R=\frac{100}{N}\left[\sum_{i=1}^{N}[(y^{\mathrm{cal}}-y^{\mathrm{expt}})/y^{\mathrm{expt}}]^2\right]^{1/2},$$

where N is the number of data points, y^{expt} is the experimental values of the surface peak, and y^{cal} is the theoretical value smoothed by polynominal fitting. The effect of the scaling factor in Ref. 6 is to put more emphasis on the asymmetry in the angular scans and less on the absolute intensity; this is roughly equivalent to letting Θ_s vary. The result for the Ag case is shown in Fig. 3. The R factor indicates a "global minimum" around $\Delta_{12}=-7.5\%$ and $\Delta_{23}=4.0\%$.

The effect of the surface Debye temperature is shown in Fig. 4 for the case of $\Delta_{12}=-7.5\%$ and $\Delta_{23}=4.0\%$. The

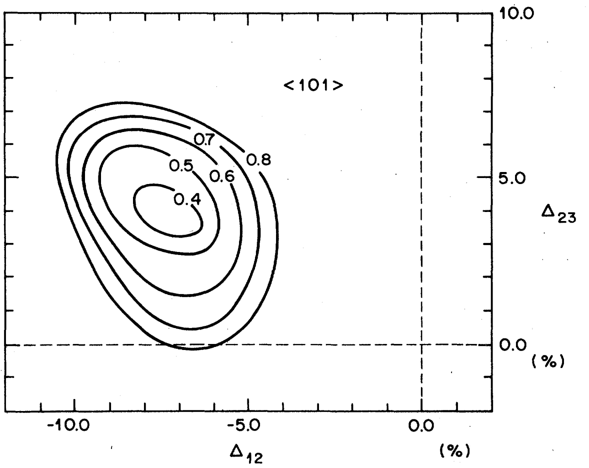

FIg. 3. Contour plot of R-factor analysis for the [101] axial data. Δ_{12} and Δ_{23} are changes of the interplanar spacing, when $\Theta_s=149$ K.

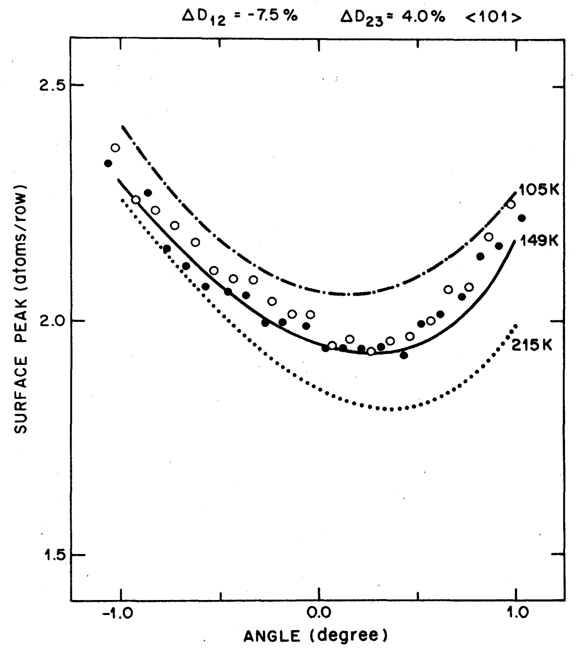

FIG. 4. Angular scan of the surface peak for [101] axis for three surface Debye temperatures: 105, 149, and 215 K, when $\Delta_{12}=-7.5\%$ and $\Delta_{23}=+4.0\%$.

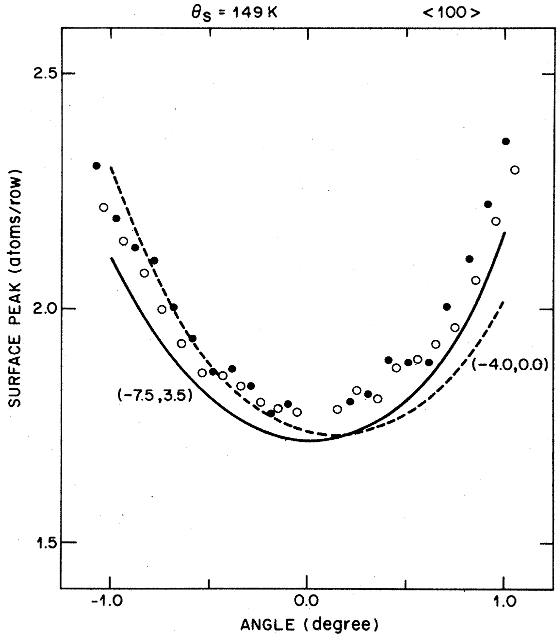

FIG. 5. Angular scan of the surface peak for the [100] axis, $\Theta_s = 149$ K.

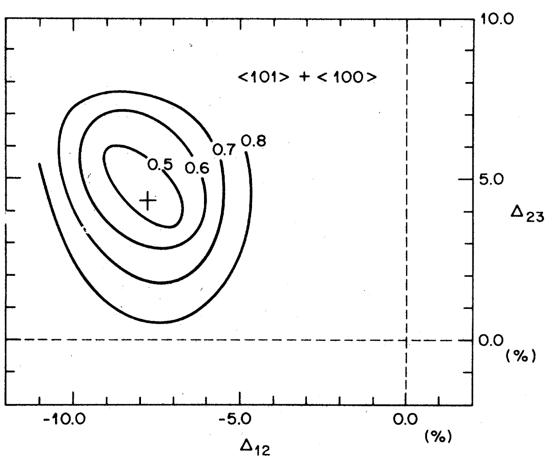

FIG. 7. Contour plot of R factor for [101] and [100] axes, as functions of Δ_{12} and Δ_{23} when $\Theta_s = 149$ K.

symmetry remains similar but the absolute yields change with surface Debye temperature. If we substitute Θ_s by 215 or 105 K, in the R-factor calculation, the R factor of the inner contour is increased from 0.40 to ~0.9.

A measurement of the angular scan was also done in the (001) plane about the [100] direction as shown in Fig. 5. In this direction there are two types of atom strings, one beginning in the surface layer and the other beginning in the second layer. The small asymmetry is a result of the cancellation of the opposite signs of the relaxation in the first two layer spacings. A large single-layer relaxation would show a large asymmetry. When we performed the R-factor analysis for the [100] direction (Fig. 6) we could not form closed contours. The effect of the cancellation is to reduce the sensitivity to extracting two unknowns, Δ_{12} and Δ_{23}, since most of the information in the experiments comes from the angular shift.

Figure 7 shows the R-factor analysis for two directions, [100] and [101], for the surface Debye temperature of 149 K. For this choice of the surface vibration, the relaxation of Ag(110) is $\Delta_{12} = -(7.8 \pm 2.5)\%$, $\Delta_{23} = 4.3 \pm 2.5\%$.

To further reveal the effect of the surface-enhanced vibration, we performed the R-factor analysis for various values of Θ_s (Fig. 8). The minimum value of the R-factor for Δ_{12} and Δ_{23} varies as a function of Θ_s although the lowest absolute value of R is for $\Theta_s = 149$ K. However, the sum of the relaxations lies along the line which has the value of $\Delta_{12} + \Delta_{23} = -3.5\%$. This implies that the absolute values of Δ_{12} and Δ_{23} are sensitive to the choice of Θ_s, but the quantity $\Delta_{12} + \Delta_{23}$ is insensitive to Θ_s.

It should be noted that $(\Delta_{12} + \Delta_{23})$ is a fundamental quantity which represents the change in spacing of the

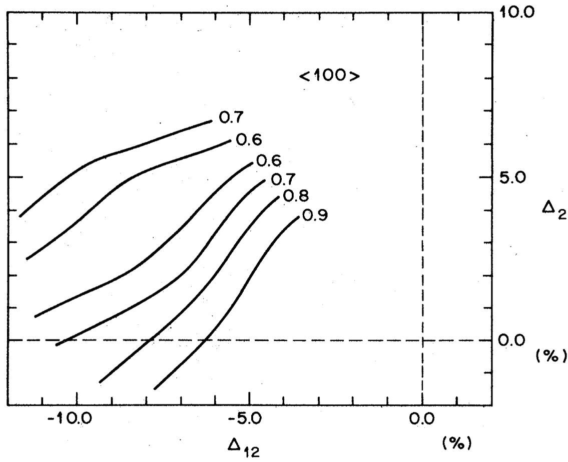

FIG. 6. Contour plot of R factor for the [100] axis, $\Theta_s = 149$ K.

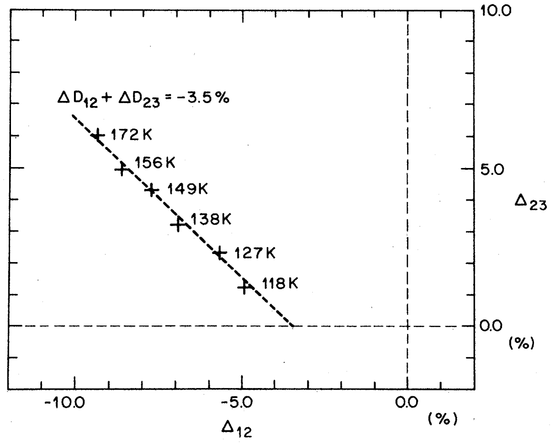

FIG. 8. Best-fit values of $\Delta_{12} + \Delta_{23}$ as a function of assumed Debye temperature. The heavy dotted line corresponds to $\Delta_{12} + \Delta_{23} = -3.5\%$.

TABLE I. Surface relaxation in various fcc crystals.

Crystal/surface	Δ_{12} (%)	Δ_{23} (%)	Δ_{13} (%)	Technique (reference)
Ni(110)	−4.8±1.7	2.4±1.2	−2.4	Ion scattering (17)
Ni(110)	−7.0			LEED (17)
Cu(110)	−5.3±2.4	3.3±1.5	−2.0	Ion scattering (6)
Cu(110)	−8.5±0.6	2.3±0.8	−6.2	LEED (6)
Ag(110)	−7.8±2.5	4.3±2.5	−3.5	Ion scattering (This work)
Ag(110)	−5.7	2.2	−3.5	LEED (12)
Ag(111)	$<\lvert 2\rvert$[a]			Ion scattering (18)
Ag(111)	No relaxation observed			LEED (19)
Pt(111)	$<\lvert 2\rvert$			Ion scattering (7)
Pt(111)	$<\lvert 0.4\rvert$			Ion scattering (20)
Pt(111)	1.5±1 (420 K)			Ion scattering (21)
Pt(111)	$<\lvert 3\rvert$			LEED (22)
Pt(111)	1 ±1			LEED (23)

[a] The absolute value signs denote that the possible direction of the relaxation, expansion, or contraction is not discernible in those cases where ion scattering sets a limit.

nearest-neighbor distance in a direction perpendicular to the surface of a fcc (110) crystal. As shown above the ion-scattering analysis provides this quantity almost independent of assumptions of surface vibrations—the vibrations are the only significant uncertainty in these types of analysis. The accuracy in $\Delta_{12}+\Delta_{23}$ is primarily a result of simple geometry, that is, the angular shifts alone represent $\Delta_{12}+\Delta_{23}$; the analysis is almost independent of the absolute magnitude of the surface peak.

Table I compares these results to other analyses which use at least two techniques for relaxation measurements. First note that the various cases show fair agreement between ion scattering and LEED (except for Ni). At this time there is no outstanding discrepancy between these two techniques for these relatively simple metal surfaces. (History demonstrates, however, that these results vary with time and such conclusions are always subject to change.) The Ag(110) and Ag(111) results are in accord with the Landman picture which predicts large relaxations for (110) surfaces and small relaxations for (111) surfaces of fcc metals. This is a particularly relevant comparison as both surfaces are measured under identical conditions by the same technique.

SUMMARY AND CONCLUSION

Energy dependences and angular scans of the surface peak for the Ag(110) surface demonstrate the existence of multilayer relaxation. The spacing between the first and second layers is contracted to (1.33±0.04) Å and the spacing between the second and third is expanded to (1.50±0.04) Å while the bulk layer spacings is 1.44 Å. The spacing between the first and third layers, which represents the nearest-neighbor spacing at the Ag surface, is contracted to 2.79 Å from the bulk value of 2.89 Å. This contraction is shown to be particularly accurate by this technique, i.e., (0.10±0.02) Å. These results are consistent with the accumulating body of data which shows large multilayer relaxations in fcc (110) surfaces.

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