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Structure of Cu(111)$p(2\times2)$Cs determined by low-energy electron diffraction

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The Cu(111)$p(2\times2)$Cs structure has been the subject of a low-energy electron-diffraction (LEED) analysis establishing that the cesium atoms occupy the on-top site relative to the copper atoms with a Cu-Cs interlayer spacing 3.01 ± 0.01 Å. The ion-core potentials of copper and cesium are calculated by means of the discrete variation method applied self-consistently to a Cu_7Cs cluster. Important points of this work are incorporation of the Cu-Cs interaction in the ion-core potential of cesium, determination of a muffin-tin potential for the adsorbed cesium atoms, and calculation of the energy dependence of the self-energy of the LEED electron. We use metric distances between spectra for finding the best agreement between theory and experiment.

I. INTRODUCTION

The present low-energy electron-diffraction (LEED) determination of the structure of Cu(111)$p(2\times2)$Cs is motivated by the interesting electronic properties of alkali adsorption systems. At less than full monolayer coverage alkali adsorbates on metals are instances of simple chemisorption systems having considerably lower work function than the clean metals.[1,2] Alkali-covered metal surfaces are of practical interest, for instance, as cathodes, promoters in heterogeneous catalysis,[3] and, recently, as charge donors in deuterium-ion sources for fusion.[4] Structure determinations of ordered alkali monolayers has so far been available only for Ni(100)$c(2\times2)$Na (Ref. 5) and for Al(100)$c(2\times2)$Na (Ref. 6).

The cesium layer of Cu(111)$p(2\times2)$Cs is close packed due to the 2:1 ratio between the atomic radii of cesium and copper. Experimental evidence indicates that close-packed monolayers of alkali atoms adsorbed on metals have similar electronic properties, but a general theoretical description is still lacking. In particular, electron-energy-loss (EEL) spectra measured by backscattered low-energy electrons show peaks associated with the excitation of plasma oscillations in the alkali layer. The characteristic loss energy depends on the coverage, and for a full monolayer the energy loss is roughly one-half of the bulk-plasmon energy, irrespective of the choice of substrate metal.[7]

Another interesting but poorly understood observation is the intense peak appearing in electron-emission spectra close below the Fermi edge, when a close-packed alkali-metal overlayer on a metal is excited by light in the near UV,[8] or is struck by excited He atoms.[9] Partly due to lack of structural information, there have been few electronic structure calculations on alkali-metal adsorption systems. Cesium-coated tungsten (001) (Ref. 10) and sodium-covered copper (111) (Ref. 11) were recently the subject of theoretical studies, though with hypothetical sites for the alkali-metal atoms.

From a LEED theory point of view Cu(111)$p(2\times2)$Cs is of particular interest since there are no previous structure determinations for this heavy, polarized adsorbate. The specific properties of the cesium atom, in particular its large electron scattering cross section, makes the design of a cesium scattering potential a crucial problem. We find that a cluster-type potential gives a much better agreement between the calculated and measured LEED spectra than a bulk metal potential. For the comparison of theoretical and experimental LEED intensities we apply metric distances[12,13] as misfit measures between beam spectra and between sets of beam spectra.

The experimental data and the potential model of the present investigation clearly indicate that cesium is located on top of copper atoms in the Cu(111)$p(2\times2)$Cs structure. The coordination-number unity is rare in the tables on the structure of metals adsorbed on metals,[14,15] where adsorbate atoms generally occupy sites with a particularly large number of nearest neighbors. The Cu—Cs bond length which is equal to the overlayer distance, is found to be 3.01 ± 0.05 Å.

Section II describes the experiment and Sec. III the calculations. In Sec. IV a comparison of theory and experiment is made. The paper is summed up in Sec. V.

II. EXPERIMENT

The measurements are made with standard three-grid LEED optics combined with a spot photometer which records the intensities of the diffraction spots on the display screen. The preparation of a copper (111) sample has been described previously.[13] Cesium is evaporated onto the substrate from a heated ampoule broken in ultrahigh vacuum. The ampoule is located in a part of the chamber which may be sealed off by a straight-through valve. We interrupt the cesium deposition by means of a shutter and make work-function and EEL measurements to check the amount deposited. As reported previously the quantities measured by these methods are sensitive to contamination and coverage.[16]

At small and intermediate coverages the adsorbate produces a ring around the specular beam spot on the LEED display. The ring-shaped diffraction pattern indicates a uniform adatom distribution on the surface.[17] During continued evaporation the ring diameter increases, and the diffraction pattern transforms to that typical of a $p(2\times2)$ overlayer. Once the $p(2\times2)$ pattern has appeared, no further changes are observed when the cesium evaporation is continued. This indicates that a Cu(111)$p(2\times2)$Cs structure is formed and that no more than one full monolayer stays on the substrate at room temperature. The nearest-neighbor distance in a $p(2\times2)$ layer of cesium on copper (111) is 5.11 Å, which is approximately twice the atomic radius of cesium, 2.6 Å.[18] The fact that the emergence energies of the low-index beams remain constant suggests that the cesium layer is not noticeably compressed upon continued evaporation.

III. ELECTRON SCATTERING POTENTIAL OF ADSORBED CESIUM

A. Potential models

The calculation of LEED from Cu(111)$p(2\times2)$Cs raises the problem of finding the charge density and the potential of an adsorbed atom that is extraordinarily large and easily deformable. The weakly bound 6*s* electrons of the cesium atoms are redistributed along the surface in a manner that is determined by the dynamic interaction between cesium and copper.

A good ion-core scattering potential for the LEED calculation should allow for the Cu-Cu, Cu-Cs, and Cs-Cs interactions, of which, in particular, the Cu-Cs interaction depends on the position of the cesium atom in the unit cell of the considered surface structure. Several lateral arrangements of cesium atoms above the atoms of the copper surface are compatible with the $3m$ symmetry of the diffraction pattern: (i) on top, (ii) bridge, equivalent to three different twofold sites occurring in patches oriented with threefold rotational symmetry, and (iii) hollow, equivalent to the threefold site with either fcc or hcp ordering of the adsorbate layer above the two top layers of the crystal.

We mimic the conceivable surface structures by clusters with the intention of getting an accurate description of the Cu-Cs interaction. We describe case (i), which is the adsorbate structure eventually found by the present LEED analysis. $Cu_{18}Cs_3$ is the smallest possible cluster that contains the Cs-Cs interaction together with the Cu-Cu and Cu-Cs interactions and has threefold symmetry about the surface normal. Since our computer is not large and fast enough for this cluster, we reduce it to Cu_7Cs. The Cs-Cs interaction, which is relatively weak, can be neglected to a reasonable approximation. Figure 1 shows one cesium atom situated 3 Å above the center of a planar hexagonal arrangement of seven copper atoms.

In parallel with the cluster models we also use a band-structure model. The purpose is to investigate to what degree the LEED analysis depends on the scattering potential of the ion cores. A self-consistent-field, linear muffin-tin orbital (SCF LMTO) band-structure calculation[19] is applied separately to solid copper and to a hypothetical fcc crystal of cesium. The interatomic distance of cesium is taken to be 5.11 Å, which is the nearest-neighbor distance in the adatom layer of Cu(111)$p(2\times2)$Cs. For cesium we include the mass-velocity and the Darwin terms.

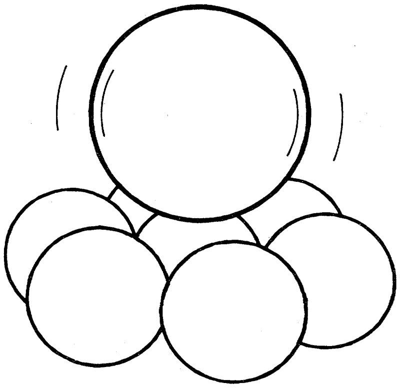

FIG. 1. Cu_7Cs cluster. For the cesium atom three radii are indicated: 1.7 Å (the Cs^{+1} ionic radius), 2.0 Å (the Cs MT radius in the present LEED calculation), and 2.6 Å [the radius of touching Cs spheres in the Cu(111)$p(2\times2)$Cs structure].

B. Cluster potential

We decide that the muffin-tin (MT) approximation, which we are forced to use in the LEED calculation, shall not intervene in the design of the adsorbate potential. We find that the discrete variation method[20–22] (DVM-$X\alpha$) calculation employed self-consistently meets the requirement mentioned. It is applicable to clusters of quite a large number of atoms and it generates a potential in a set of points distributed densely over the cluster.

Our DVM-$X\alpha$ calculation of the charge density of Cu_7Cs uses a linear combination of atomic orbitals composed of free-atom wave functions integrated numerically.

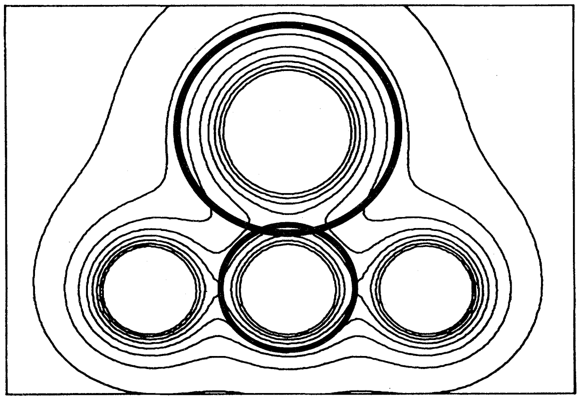

FIG. 2. Equipotential contours in the plane containing one cesium and three copper atoms. Contours are drawn in 4-eV steps between −28 and 0 eV. The bold-line circles illustrate the MT's of copper and cesium of radii 1.28 and 2.0 Å.

During all stages of the self-consistent calculation the cores of cesium and copper are treated as frozen and the valence states are kept orthogonal to the core states. Relativistic effects are not included. The exchange-correlation part of the cluster potential is approximated by the $X\alpha$ model with $\alpha=0.7$. The C_{6v} symmetry of Cu_7Cs is utilized for condensing the basis set of molecular orbitals; 9000 integration points are used by the DVM.

We start from the valence states $5p^6 6s^1 6p^0$ for cesium and $3d^{10}4s^1 4p^0$ for copper, and self-consistency is attained with the configurations $5p^{5.87}6s^{0.01}6p^{0.04}$ and $3d^{9.92}4s^{0.90}4p^{0.34}$ after 20 iterations. The occupation numbers for copper are in reasonable agreement with $3d^{9.56}4s^{0.70}4p^{0.76}$ as obtained by the band-structure model mentioned in Sec. III A. Figure 2 visualizes the cluster potential by contours of equal potential energy drawn at every 4 eV in the range -28—0 eV. The figure shows the position of the saddle point in the potential on the line joining cesium and the nearby copper atom. Later we use this point as a start when searching a MT radius for cesium (Sec. IV A).

A Mulliken population analysis[23] shows that the cluster calculation ends up with a $Cs^{+1.1}$ ion. This indicates that the Cu_7Cs cluster corresponds to low-coverage adsorption of cesium, in agreement with work-function and EEL measurements (Sec. II) showing that a single cesium atom is fully ionized by the contact with the copper surface.

C. Inner potential

A general requirement set by the LEED application is that the ion-core potentials of the adsorbate and the substrate have to be of the excited-state type. The inner potential increases by roughly 5 eV over the energy range 10—150 eV, where our LEED spectra from cesium on copper are recorded, while the measurement positions the diffraction peaks well within 1 eV. Earlier LEED investigations of aluminum,[21] oxygen on aluminum,[21] and copper[13,22] indicate that the local-density approximation of Hedin and Lundqvist[24] accurately describes the energy dependence of the ion-core potential. Specifically, since the existing LEED programs[25–28] are based on the Korringa-Kohn-Rostoker (KKR) concept, the ion-core potentials have to be available in the MT form.

We apply the local-density excited-state scheme described in Ref. 21 and compose an excited-state potential whose Hartree part equals the Hartree part of the ground-state potential and whose exchange-correlation part corresponds to the self-energy of the LEED electron in a locally homogeneous electron gas. The density of this gas is approximated by the ground-state density.

When converted to the MT form the ion-core potentials of copper and cesium have the MT radii r_{Cu} and r_{Cs} and the potentials $V_{0\,Cu}$ and $V_{0\,Cs}$ on the MT boundary. We consider the central copper atom in the Cu_7Cs cluster. r_{Cu} is put equal to the radius of touching spheres in the copper lattice, 1.28 Å, and the MT potential is shifted so that $V_{0\,Cu}$ becomes equal to the interstitial potential of fcc copper. From a recent measurement[13,29] of the subthreshold effect in LEED from copper (111) we infer $V_{0\,Cu}=-7.5$ eV relative to the Fermi level.

For the cesium atoms, having empty space on one side and a copper layer on the other, there is no simple geometrical argument to determine a MT, and r_{Cs} and $V_{0\,Cs}$ have to be treated as adjustable parameters during the LEED analysis. Before setting up a test grid for r_{Cs}, we calculate the potential of Cu_7Cs on the line joining the cesium nucleus and the nucleus of the central copper atom. There is a saddle point at the cesium radius, 1.7 Å, which is also the tabulated radius[18] of Cs^{+1}.

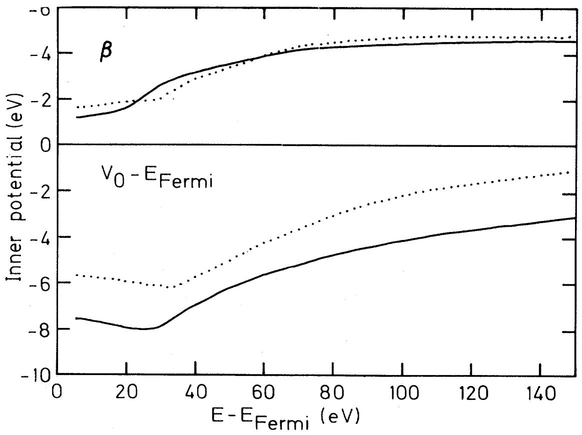

FIG. 3. Inner potential $V_0+i\beta$ for copper (——) and cesium (····) vs the energy of the incident electron.

The energy-dependent inner potentials of the copper substrate and the cesium adlayer are shown by the V_0-vs-E diagrams in Fig. 3 ($r_{Cu}=1.28$ Å and $r_{Cs}=2.0$ Å). The absorptive potentials $\beta(E)$ drawn in the same diagram are phenomenological curves obtained by a fit of the calculated LEED spectra to the measured ones.

IV. LEED ANALYSIS

A. LEED calculation

The LEED analysis is made by means of a layer KKR computer program, which uses the layer-doubling scheme for the interlayer scattering[25] and which applies automatic symmetrization to the plane-wave and the angular-momentum representations of the wave field.[26] The symmetrization is extremely important as a time-saving device

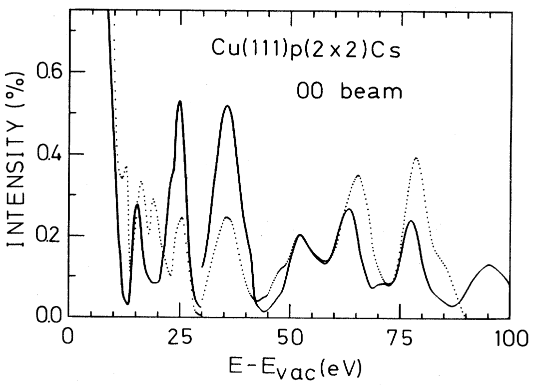

FIG. 4. 00 spectrum from Cu(111)$p(2\times2)$Cs at 4° off-normal incidence for experiment (——) and calculation (····). Cu-Cs interlayer spacing is 3.01 Å.

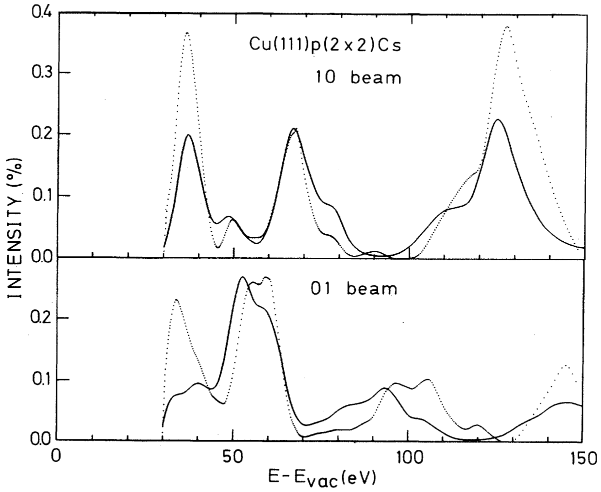

FIG. 5. 10 and 01 spectra from Cu(111)$p(2\times2)$Cs at normal incidence for experiment (——) and calculation (· · · ·). Experimental 10 spectrum has been multiplied by 0.7.

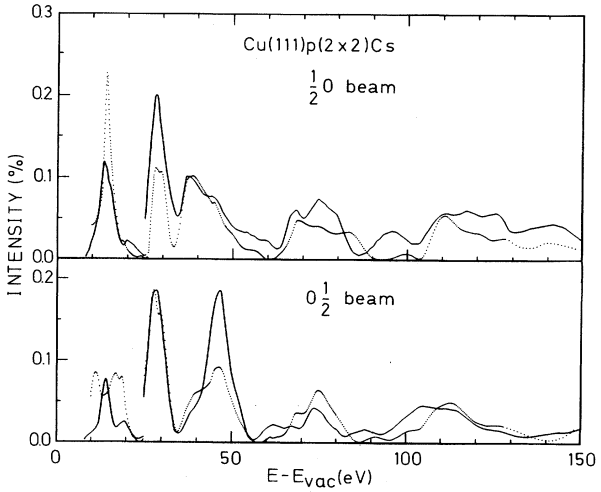

FIG. 6. $\frac{1}{2}$0 and 0$\frac{1}{2}$ spectra from Cu(111)$p(2\times2)$Cs at normal incidence for experiment (——) and calculation (· · · ·). Experimental spectra are multiplied by a factor 1.6 and 1.3, respectively.

in connection with the present overlayer structure. Not only does Cu(111)$p(2\times2)$Cs give rise to 4 times as many diffraction spots as clean copper (111), but cesium is also a strong electron scatterer demanding roughly twice as many phase shifts as copper at a given energy. The program takes ten phase shifts which are sufficient to describe the electron scattering by cesium up to an energy of the order of 150 eV.

When varying the Cu-Cs layer spacing between 2.5 and 4.5 Å for the adsorption sites (i)—(iii) described in Sec. III A, we find that exclusively the on-top site agrees convincingly with the experiment. It is manifest that the cluster potential gives rise to a superior LEED description in comparison with the band-structure model. The best fit is obtained with an unrelaxed (111) surface of copper. The overlayer separation, which in this case is the same as the Cu—Cs bond length, turns out to be 3.01±0.5 Å. Figures 4—6 show measured and calculated spectra for the 00 beam, the 10 and 01 beams, and the $\frac{1}{2}$0 and 0$\frac{1}{2}$ beams.

The LEED analysis gives $r_{\mathrm{Cs}}=2.0$ Å, a value intermediate between the saddle-point radius, 1.7 Å, and half the nearest-neighbor distance in the $p(2\times2)$Cs layer, 2.5 Å. With $r_{\mathrm{Cu}}=1.28$ Å and $r_{\mathrm{Cs}}=2.0$ Å the MT's of copper and cesium overlap by 0.2% of the copper volume or by 0.05% of the cesium volume. The calculated spectra are found to be highly affected by a shift of the cesium potential, particularly for very low energies: We use $V_{0\,\mathrm{Cs}}=-5.5$ eV relative to the Fermi level. The sensitivity with respect to $V_{0\,\mathrm{Cu}}$ can be related to the fact that cesium has a resonance in the f-phase shift at about 30 eV.

The choice of the Debye temperature Θ_D and the absorptive potential β for cesium proves greatly to influence the LEED analysis. For copper we take $\Theta_D=300$ K and use the same β curve as in an earlier LEED study of clean copper[13] (see Fig. 3). For solid cesium Θ_D is 38 K.[18] The best agreement with the LEED experiment is obtained for different Debye temperatures, 60 and 180 K, for the thermal motions parallel and orthogonal to the surface. The result indicates that the Cu—Cs bonding is substantially stronger than the Cs—Cs bonding. Our LEED analysis indicates that the absorptive potential β of cesium is somewhat different from that of copper (see Fig. 3).

In some energy regions the calculated spectra prove particularly sensitive to the Cs-Cu interlayer spacing d. The 00 spectrum (Fig. 4) has a peak standing on the interval 30—40 eV where the corresponding spectrum of clean copper (111) vanishes.[13] Interference between the adsorbate layer and the substrate creates this peak, and it alone would determine the overlayer spacing, provided that the inner potential (and hence the electron wavelength) were available from a separate measurement. In the 10 spectrum (Fig. 5) the peak near 37 eV moves rapidly out of place when d is varied from 3.01 Å, and in the 01 spectrum the shape of the predominant peak at 55 eV is strongly affected by a variation of d. In the $\frac{1}{2}$0 spectrum (Fig. 6) the slope between 38 and 60 eV is well reproduced only for $d=3.01$ Å, and in the 0$\frac{1}{2}$ spectrum the balance between the peaks at 28 and 46 eV changes dramatically against variations of d.

B. Metric distances between spectra

A misfit measure between the theoretical and the experimental spectra should be sensitive to the different peaks, which provide the information about the composition of the surface unit cell, and, preferably, ignore the slow energy variations having a nonstructural origin. In the present investigation these variations are not quite the same in the theory and in the experiment. Possible explanations are that the LEED theory employs a temperature factor[25] which we believe is very approximate for a Debye temperature as low as that of cesium on copper, and that the experimental beam intensities decrease with energy not only by thermal attenuation but also by surface imperfections. A treatment of the spectra by means of a Fourier high-pass filter is found to detach the diffraction peaks from the slow energy variations. We compare the calcu-

TABLE I. Metric analysis of the 00, 10, 01, $\frac{1}{2}0$, and $0\frac{1}{2}$ spectra. E_1—E_2 is the range of comparison, d is the Cu-Cs interlayer spacing, ΔV_0 is a common shift of the inner potentials of copper and cesium, and T is the minimum value of the total metric. The metrics are 1 (strong integrated), 2y (weak integrated), 3y (Levy), and 4y (Hausdorff).

E_2[a] (eV)	d (Å) 1	2y	3y	4y	ΔV_0 (eV) 1	2y	3y	4y	T (%) 1	2y	3y	4y
					Crude data							
70	2.95	2.95	2.97	2.97	0.0	0.5	1.5	1.5	20	4.1	7.0	7.4
90	3.00	2.94	2.93	2.95	0.5	1.0	2.0	2.0	22	4.4	7.2	7.6
110	3.03	3.10	3.03	3.04	1.0	3.0	2.5	2.0	24	3.7	6.6	6.9
130	2.99	3.08	3.08	3.07	0.5	3.0	2.0	2.0	25	3.7	7.3	7.9
150	3.04	3.04	3.06	3.06	1.0	1.5	1.5	1.5	22	4.0	6.9	7.4
					High-pass filtered data							
70	2.98	2.95	2.90	2.90	0.5	0.0	0.0	0.0	11	1.3	2.6	2.9
90	2.99	3.00	2.97	2.97	0.5	2.0	2.0	0.5	13	1.5	2.9	3.3
110	2.98	3.01	2.93	2.95	0.5	1.0	0.5	1.5	14	1.5	3.2	3.5
130	3.00	3.00	2.98	2.98	0.5	1.0	0.5	0.5	13	1.3	2.8	3.0
150	3.02	3.02	3.00	3.00	0.5	0.5	0.5	0.5	13	1.4	2.6	2.9

[a] $E_1 = 13$, 30, 42, 10, and 24 eV for the 00, 10, 01, $\frac{1}{2}0$, and $0\frac{1}{2}$ spectra. $E_2 \leq 90$ eV for the 00 spectrum.

lated and measured spectra (filtered or unfiltered) using the method of metric distances proposed by Philip and Rundgren.[12]

In Table I the calculated and measured spectra are compared by means of four metrics applied both to the crude and to the filtered spectra. We apply the same types of metric to the spectra from Cu(111)$p(2\times2)$Cs as in a previous paper[13] on clean copper (111). At very low energies the calculated spectra exhibit portions of high intensity which are dissimilar to the measurement whatever input parameters we choose. As we are forced to exclude these portions from the analysis, we make the metric comparisons over energy ranges E_1—E_2, where E_1 depends on the beam under study (see the footnote of Table I). We investigate to what extent the metric distances depend on energy ranges by varying E_2.

Looking at the total metric distances in Table I we observe that the agreement is improved when the diffraction peaks are enhanced by Fourier high-pass filtering, and we therefore determine the Cu-Cs interlayer spacing d from the lower part of the table. It turns out that the total metric distances remain practically the same when E_2 is increased from 70 to 150 eV. In principle, the largest possible data base is preferred in a LEED investigation, and we infer the Cu-Cs interlayer spacing d from the last line of Table I. We set error bounds such that they comprise most of the energy ranges and most of the metrics for both the crude and the filtered data, and find that the Cu-Cs spacing is 3.01±0.05 Å. The shift ΔV_0 is so small that we are apt to believe that the inner potentials of Fig. 3 are correct within the limit of error of the proposed potential model.

V. SUMMARY

The LEED calculations on Cu(111)$p(2\times2)$Cs are based on cluster models for the electron scattering potentials of copper and cesium, and we find that the cesium potential is significantly influenced by the Cu-Cs interaction. The considered energy range is 10—150 eV, and it proves absolutely necessary that the inner potential and the scattering phase shifts have a consistent energy dependence. This we calculate from local-density excited-state potentials using the Hedin-Lundqvist scheme. The comparison of theoretical and experimental spectra is made by means of metric distances between spectra.

We find that the cesium atoms occupy on-top positions with a Cs—Cu bond length 3.01±0.05 Å. Subtracting the hard-sphere radius of copper, 1.28 Å, we find that the effective radius of cesium is 1.73±0.05 Å. Within the error bounds the effective radius of cesium in the Cu(111)$p(2\times2)$Cs structure equals the tabulated Cs^{+1}-ion radius.

The outcome that the cesium adatom takes the on-top site relative to the copper substrate is an exception from "this tendency towards occupying the site with the largest coordination number during adsorption on metals."[30] As far as we know the Cu(111)$p(2\times2)$Cs structure is the first instance found where a metal adsorbs on a metal with a coordination-number unity.

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