Determination of the atomic geometries of the (110) surfaces of CuCl and CuBr by dynamical low-energy electron diffraction intensity analysis

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The atomic geometries of the nonpolar (110) surfaces of CuCl and CuBr are determined by dynamical analysis of the intensities of 13 diffracted beams for CuCl and 16 beams for CuBr associated with normally incident electrons at T=125 and 100 K, respectively. The structural model is specified by six independent variables consisting of the tilt angles (ω_i) of the top two layers, the three independent bond lengths ($c_i - a_i$) associated with atoms in the top two layers, and the inner potential. The focus of our analysis is the accuracy and precision with which these six structural parameters can be extracted from the measured intensities. A six-dimensional statistical error analysis was performed for two electron-solid scattering models: one model in which all nonstructural parameters assumed the values used in a family of previous structural analyses for the (110) surface of CuCl and other binary zinc-blende structure materials, and one in which these parameters were treated as adjustable parameters to fit the measured intensities. The structural parameters emanating from these two analyses differ by $\Delta\omega \leq 4^{\circ}$ and $\Delta(c_i - a_i) \leq 0.3$ Å. Statistical analysis of uncertainties in the structural parameters resulting only from uncertainties in the measured intensities yields $\Delta \omega \leq 1.3^\circ$, $\Delta (c_i - a_i) \leq 0.02$ Å. Thus, the uncertainties in the structural parameters associated with the selection of the nonstructural parameters, especially the model of the electron exchange interaction, dominate those associated with the uncertainties in the experimental intensity data. Within these uncertainties we find the top-layer bond lengths are contracted by 0.3 Å for CuCl(110) and 0.1 Å or less for CuBr(110). Changes in the backbonds from the anion and cation cannot be established for CuCl using the existing intensity data in our analysis. For CuBr(110) the backbond from the top-layer cation is contracted by 0.35 ± 0.2 Å. The tilt angles are $\omega_1 = (53\pm2)^\circ$ for CuCl and $(35\pm2)^{\circ}$ for CuBr with $\omega_2 = (-5\pm1)^{\circ}$ for both. These results are compatible with previously identified structural systematics that the most ionic zinc-blende structures exhibit top-layer bond-length contractions which increase their tilt angles relative to the value of $(29\pm3)^{\circ}$ characteristic of bond-length-conserving rotational relaxations of covalent III-V and II-VI (110) surfaces. [S0163-1829(96)05244-7]

I. INTRODUCTION

For several decades the nature of the dependence of the surface atomic geometries of the (110) nonpolar cleavage faces of zinc-blende structure compound semiconductors on bulk parameters describing the nature of the chemical bonding has been debated intensely.¹⁻⁸ After considerable discussion it was shown^{5,9-11} that the surface structures of the (110) surfaces III-V and II-VI compounds are approximately bond-length-conserving rotations in which all structural parameters scale linearly with the bulk lattice constant a_0 . It was still argued,^{3,4} however, that the more ionic I-VII compounds, CuCl, CuBr, and CuI in particular, represent an extreme in which ionic bonding dominates covalent bonding and hence the approximately bond-length-conserving "covalent" relaxation would collapse in these materials. In a preliminary analysis of low-energy electron diffraction (LEED) intensities from CuCl(110), Kahn et al.⁶ showed that this expectation was not met for CuCl. Subsequently, Lessor et al.⁷ suggested on the basis of a similar analysis that the main effect of the increasing ionicity of the surface bonding in the isoelectronic series GaP-ZnS-CuCl was to decrease the length of the surface anion-cation bond by reducing the lateral relaxation of the anion: a notion subsequently supported by local-density-functional calculations of the surface structure.⁸ Our purpose in this paper is to present a comprehensive LEED intensity analysis of CuCl(110) and CuBr(110) that confirms and refines the earlier analyses of CuCl (Refs. 6 and 7) as well as provides a quantitative estimate of the degree of surface bond-length change that can be extracted reliably from such an analysis.

The vehicle that we utilize to perform a surface structural analysis with the accuracy and precision required to determine small surface bond-length changes is a statistical uncertainty analysis methodology recently introduced by Duke et al.¹² Its application to the (110) surfaces of CuCl and CuBr revealed, however, an unexpected result: The structural results may depend sensitively on seemingly innocuous variations in the model chosen for the exchange interaction. Because of the potential importance of this result for the assessment of uncertainties in the surface structural parameters via LEED intensity analyses, we document it in some detail. Its major implication for our structural model is that the uncertainties in the surface bond lengths may be as much as an order of magnitude larger than those predicted on the basis of uncertainties in the LEED intensity data alone. Uncertainties in the tilt angles of the chains of atoms in the upper layers are increased only by a factor of about 2.

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FIG. 1. Rigid lattice phase shifts for the atomic species (a) Cu, (b) Cl, and (c) Br used in the structure determinations of the CuCl(110) and CuBr(110) surfaces. The atomic potentials were calculated including spin-orbit coupling and a Slater exchange parameter X_a of 1.0. The Slater exchange was removed in the crystal potential calculation and Hara energy-dependent exchange was added before calculating the phase shifts. The muffin-tin radii for the three species were Cu in CuCl=1.148 Å, in CuBr=1.170 Å; Cl=1.192 Å; Br=1.294 Å. The crossover potentials were -6.604 eV and -6.502 eV, for CuCl and CuBr, respectively.

We proceed by describing the sample preparation and data acquisition in Sec. II. In Sec. III A we indicate the construction of the electron-solid interaction and the calculation of the LEED intensities. Section III B contains a description of the structure search and error analysis. Our results for the (110) surfaces of CuCl and CuBr are presented in Sec. IV and discussed in Sec. V.

II. SAMPLE PREPARATION AND DATA ACQUISITION

The LEED measurements reported in this work were performed on the (110) surfaces of thin CuCl and CuBr layers epitaxially grown on the (110) surfaces of isoelectronic III-V GaP and GaAs, respectively. The two pairs of compounds exhibit a similar lattice mismatch, with the lattice constant of



FIG. 2. Rigid lattice phase shifts for the atomic species (a) Cu, (b) Cl, and (c) Br used in the structure determinations of the CuCl(110) and CuBr(110) surfaces. The atomic potentials were calculated including spin-orbit coupling and a Slater exchange parameter X_a of 0.6. The Slater exchange was removed in the crystal potential calculation and Hara energy-dependent exchange was added before calculating the phase shifts. The muffin-tin radii for the three species were Cu in CuCl=1.148 Å, in CuBr=1.173 Å; Cl=1.193 Å; Br=1.291 Å. The crossover potentials were -10.32eV and -10.09 eV, for CuCl and CuBr, respectively.

the I-VII compound larger by 0.8% in the CuCl-GaP pair and 0.7% in the CuBr-GaAs pair.

The GaP and GaAs crystals were first oriented and cut along the (110) plane, mechanically polished with 1- μ m SiC powder, and chemically polished with a 0.5% solution of bromine in methanol until both surfaces exhibited a mirrorlike finish. After being placed in ultrahigh vacuum (UHV), the GaP and GaAs surfaces were bombarded with 2-keV Ar⁺ to remove contaminants, and annealed at 500 °C and 600 °C, respectively, for 5 min to restore atomic order. Both surfaces produced sharp (1×1) LEED patterns indicative of longrange atomic order.

CuCl and CuBr were grown *in situ* with similar conditions of evaporation and condensation. The I-VII compounds were evaporated congruently from solid sources consisting



FIG. 3. Planar side-view projection of the zinc-blende(110) surfaces illustrating the independent surface structural parameters expressed as bond lengths, $c_i - a_j$, and chain tilt angles, ω_i . The symbol $c_i - a_j$ designates the bond length between the cation in the *i*th layer and the anion in the *j*th layer. ω_i designates the tilt angle (relative to the unrelaxed surface) of the planar zigzag chains in the *i*th layer.

of high-purity CuCl or CuBr powder (99.9%, Johnson Matthey Electronics) placed in a quartz crucible and heated to 200 °C. 300-Å-thick layers were grown on the substrates at a nominal rate of 29 Å/min and with an optimized substrate temperature of 100 °C in both cases. Lower growth temperatures produced poor epitaxy, and higher temperatures led to reduced sticking coefficients, faceting, and increased interfacial chemical reactions, leading to the formation of interface layers of Cu₃P or Cu₃As. The I-VII surfaces were optically smooth and produced sharp (1×1) LEED patterns with the twofold (hk)=(-hk) symmetry of the zinc-blende (110) unit cell. For both I-VII/III-V pairs the pattern of the epitaxial layer was found to be precisely aligned with that of the substrate, indicating that the I-VII unit cell was azimuthally aligned with the III-V unit cell (±180°).

The intensity versus energy (I-V) profiles were recorded with a fast LEED data acquisition system, which allowed us



FIG. 4. Traditional independent structural variables used to describe zinc-blende (110) surfaces. (a) Side view; (b) top view.

to limit the integrated time of exposure of the surface to the electron beam to about 10 min with a beam current $\leq 1 \mu A$. For CuCl I-V profiles of 13 nonequivalent diffracted beams, i.e., the (01), (0-1), (11)=(-11), (-1-1)=(1-1), (10) =(-10), (02), (0-2), (12)=(-12), (1-2)=(-1-2), (20)=(-20), (21)=(-21), (03), and (0-3) were recorded in normal incidence condition in energy steps of 2 eV for energies ranging between 33 and 180 eV. In the CuBr case, 16 beams, i.e., the (01), (0-1), (11)=(-11), (1-1)=(-1-1), (10) =(-10), (02), (0-2), (12)=(-12), (1-2)=(-1-2), (20)=(-20), (-21)=(21), (03), (0-3), (2-1)=(-2-1), (13)=(-13), and (1-3)=(-1-3) were measured over energy ranges between 16 and 310 eV, also in 2-eV steps. Two sets of I-V profiles were collected for each compound and averaged to reduce the statistical noise in the data. All LEED measurements were taken with the sample cooled (to \sim 125 K for CuCl and \sim 100 K for CuBr) in order to reduce the thermal atomic vibrations in the low Debye temperature I-VII compounds ($\theta_D \approx 180$ K at room temperature¹³).

TABLE I. Gaussian and x-ray r factors for CuCl(110) vs structural and nonstructural parameters. The notation $c_2 - a_1$ indicates the bond length between the cation in the second layer (bilayer if ω_2 is nonzero) and the anion in the first (surface) "bilayer," etc. All bond lengths, Δ 's, and λ_{ee} are in angstroms. The R_x and R_1 values for the unrelaxed structure and the "best fit" from Ref. 6 are different from those reported in Ref. 6. This is because we now use an exponential grid to construct the phase shifts, rather than the uniform grid used to generate Ref. 6. The value of V_0 for the unrelaxed calculation was not optimized.

Structure	ω_1 (deg)	$\Delta_{1,\!\perp}$	ω_2 (deg)	$\Delta_{2,\perp}$	$c_2 - a_1$	$c_1 - a_1$	$c_1 - a_2$	X_{α}	$\langle u^2 \rangle$	V_0 (eV)	λ_{ee}	R'_2	R_x	R_l
Unrelaxed	0.00	0.00	0.00	0.00	2.341	2.341	2.341	1.0	0.0306	10.00	8	0.28	0.19	0.23
"Best" fit from Ref. 6	41.25	0.68	0.00	0.00	2.419	2.169	2.252	1.0	0.0306	9.00	8	0.25	0.18	0.05
"Best" one-layer relaxation	45.93	0.74	0.00	0.00	2.446	2.171	2.230	1.0	0.0306	10.39	8	0.23	0.19	0.04
"Best" two-layer relaxation with old nonstructural parameters	51.03	0.79	-4.14	0.10	2.367	2.163	2.181	1.0	0.0306	12.93	8	0.16	0.19	0.05
"Best" two-layer relaxation with new nonstructural parameters	55.44	0.78	-5.53	0.13	2.310	2.131	2.374	0.6	0.0300	11.41	9	0.14	0.14	0.07

TABLE II. Effect of nonstructural parameters on the Gaussian r factor for a CuCl(110) structure proposed by Lessor *et al.* (Ref. 7). This structure was used as the starting point for the subsequent two-layer relaxations. V_i is the imaginary complex optical potential defined using $\Sigma = -V_0 - iV_i$ in lieu of Eq. (1).

$\overline{X_{\alpha}}$	$\langle u^2 \rangle$	V_i	λ_{ee}	R'_2
1.0	0.03	4.20	0	0.26
0.6	0.03	4.20	0	0.18
0.6	0.04	3.7	0	0.17
0.6	0.04	0	9	0.17
0.6	0.03	0	9	0.17

III. DATA ANALYSIS

A. Calculation of the LEED intensities

The LEED intensity data were analyzed using the method of Laramore and Duke.¹⁴ This dynamical multiple-scattering LEED theory is a generalization of the work of Beeby¹⁵ in which a complex electron self-energy has been included.¹⁶ The computer programs used to perform the calculations are modularized extensions of those described in earlier analyses of the (110) surface structure of GaAs.^{17,18} These programs and the procedure used to construct the model of the electron-solid interaction have been used to determine the atomic geometries of the (110) surfaces of all zinc-blende structure binary III-V and II-VI semiconductors^{5,11,19} and have been applied previously in an analysis of LEED from CuCl.⁶ Thus, the calculational methodology has been thoroughly tested for the application to the analysis of LEED from the (110) surfaces of zinc-blende structure I-VII compounds.

Electron scattering by surface atoms is described using energy-dependent phase shifts. Each atomic scattering center is represented as a neutral atom whose potential is first computed using a relativistic, self-consistent Hartree-Fock-Slater muffin-tin model.^{20,21} For calculating the scattering phase shifts of the LEED electrons, however, the Slater $\rho^{1/3}$ exchange term of the computed self-consistent atomic potential is replaced by an energy-dependent Hara exchange term²² in the calculation of the phase shifts. The Hara exchange model has been shown to describe better the physics of electron scattering in LEED, where external electrons with energies greater than 10 eV above the Fermi level interact with the electron cloud at the surface.^{20,23} The resulting effectivescattering potential is inserted into the radial Schrödinger equation, which is integrated to yield the scattered wave phase shifts. These phase shifts depend on the coefficient X_{α} of the $\rho^{1/3}$ exchange term used to obtain the neutral atom potential. Phase shifts associated with $X_{\alpha}=1$ and 0.6 are shown in Figs. 1 and 2, respectively. This becomes an important point in our structure analyses because the quality of the fits to the data and the resulting values of the structural parameters depend upon the value of X_{α} .

Thermal vibrations of the atoms are incorporated into the analysis via an imaginary part of the phase shifts²⁴ calculated as described by Duke *et al.*²⁵ The magnitudes of these vibrations were estimated by optimizing the description of the experimental LEED intensities for our final model of the imaginary part of the one-electron optical potential. This procedure yielded $\langle u^2 \rangle_{Cu} = \langle u^2 \rangle_{Cl} = \langle u^2 \rangle_{Br} = 0.03 \text{ Å}^2$ for both CuCl and CuBr.

The influence of electron-electron interactions on the propagation of the incident electron between the muffin-tin ion cores is described by the complex one-electron propagator²⁶

$$\Sigma(E) = -V - i\hbar [2m(E+V_0)]^{1/2} / m\lambda_{ee}.$$
 (1)

In our initial calculations, we utilized $\lambda_{ge} = 8$ Å for compatibility with our earlier analysis of CuCl.⁶ The real-part of the "inner potential" V_0 was treated as a variable to be determined during the structure analysis because values of some of the structural parameters are strongly correlated with that of V_0 .^{27,28} Ultimately, we also treated the imaginary part $\Sigma(E)$ as a variable in fitting the LEED intensity data, using both Eq. (1) and a constant imaginary part, $-iV_i$.

In the LEED intensity calculations, each atomic layer parallel to the surface was divided into one Cu and one Cl (or Br) sublattice. The scattering amplitudes for each sublattice were evaluated analytically whereas the scattering between sublattices was described by a set of coupled matrix equations. These equations were solved exactly for the top six layers. For deeper layers, the scattering amplitudes for each layer were obtained by considering the multiple scattering between the two sublattices within the layer but neglecting the multiple scattering between layers. For $\lambda_{ee} = 8$ Å, explicit checks revealed that the calculated intensities were converged to within a few percent for the six-layer exact treatment. For our initial structural searches for CuCl we used the nonstructural parameters characteristic of our prior study,⁶ i.e., $X_{\alpha} = 1$, $\langle u^2 \rangle = 0.03$ Å, and $\lambda_{ee} = 8$ Å. For our initial structural searches for CuBr(110), we selected $\lambda_{ee} = 8$ Å and the values of $\langle u^2 \rangle_{Cu} = \langle u^2 \rangle_{Br} = 0.0178 \text{ Å as a compromise between}$ slightly better fits to the data and practically feasible multiple parameter structural searches. Once we obtained a structure

TABLE III. Covariance matrix for the "best" two-layer relaxation of CuCl(110) specified in row 5 of Table I. The diagonal elements are an estimate of σ^2 for the labeled parameter.

	ω_1	ω ₂	$c_2 - a_1$	$c_1 - a_1$	$c_1 - a_2$	V_0
$\overline{\omega_1}$	1.637×10^{0}	-8.328×10^{-3}	5.413×10^{-3}	-4.828×10^{-3}	1.468×10^{-2}	-1.628×10^{-2}
ω_2	-8.328×10^{-3}	1.289×10^{-1}	-1.308×10^{-3}	1.149×10^{-4}	-4.221×10^{-4}	1.613×10^{-2}
$c_2 - a_1$	5.413×10^{-3}	-1.308×10^{-3}	1.181×10^{-4}	-2.416×10^{-5}	-2.960×10^{-5}	-6.643×10^{-4}
$c_1 - a_1$	-4.828×10^{-3}	1.149×10^{-4}	-2.416×10^{-5}	3.742×10^{-5}	-6.330×10^{-5}	-1.167×10^{-4}
$c_1 - a_2$	1.468×10^{-2}	-4.221×10^{-4}	-2.960×10^{-5}	-6.330×10^{-5}	3.017×10^{-4}	-1.798×10^{-4}
V_0	-1.628×10^{-2}	1.613×10^{-2}	-6.643×10^{-4}	-1.167×10^{-4}	-1.798×10^{-4}	2.528×10^{-2}

TABLE IV. Correlation matrix associated with the covariance matrix in Table III.

	ω_1	ω_2	$c_2 - a_1$	$c_1 - a_1$	$c_1 - a_2$	V_0
ω_1	1	-1.813×10^{-2}	3.893×10^{-1}	-6.170×10^{-1}	6.604×10^{-1}	-8.004×10^{-2}
ω_2		1	-3.353×10^{-1}	5.231×10^{-2}	-6.769×10^{-2}	2.825×10^{-1}
$c_2 - a_1$			1	-3.634×10^{-1}	-1.568×10^{-1}	-3.844×10^{-1}
$c_1 - a_1$				1	-5.958×10^{-1}	-1.200×10^{-1}
$c_1 - a_2$					1	-6.512×10^{-2}
V_0						1

leading to a sufficiently low R factor, however, we treated X_{α} , $\langle u^2 \rangle$, and the imaginary part of the potential as variables used to optimize the description of the LEED data.

B. Structure analysis

The present structure analysis differs from most of its predecessors^{11,19} for zinc-blende (110) surfaces in three respects. First, since bond-length changes are expected for the ionic I-VII compounds,^{6,7} we utilize bond lengths and tilt angles directly as the independent structural variables^{18,29} as indicated in Fig. 3. Second, since we are providing a statistically significant uncertainty analysis, we utilize the "Gaussian" R factor, R'_2 defined and discussed by Duke et al.,¹² as the figure of merit determining the goodness of fit between the calculated and measured intensity profiles. For purposes of comparison with prior results, we also give the values of the x-ray³⁰ and integrated intensity³¹ R factors used previously. The best fit structures are determined, however, by minimizing R'_2 . Third, we explore systematically the influence of the nonstructural parameters, e.g., X_{α} , $\langle u^2 \rangle$, and λ_{ee} , both on the quality of the fits to the LEED intensity data and on the optimal structural parameters. We find a significant, previously unexplored, dependence of the optimal structure on the value of the exchange coefficient X_{α} used in constructing the atomic potentials.

The mapping of structural variables from the bond-length representation (Fig. 3) into the traditional independent variables representation (Fig. 4) is indicated in the Appendix. The cubic unit cell parameters, a_0 , designated as a_y in panel (b) of Fig. 4, are taken to be 5.406 and 5.691 Å for CuCl and CuBr, respectively.³² From the perspective of precise structure determination, the traditional variables given in Fig. 4 are preferable because they tend to be weakly correlated with each other and some of them (e.g., $\Delta_{1\perp}$) are even weakly correlated with the inner potential V_0 :³³ a fact exploited in establishing scaling laws between different materials.⁹ Since we are searching for trends in the bond lengths with ionicity, however, we utilize a coordinate system are the ones shown in Fig. 3 (Refs. 18 and 29) or an analogous one with ω_1 and ω_2 replaced by $\Delta_{1\perp}$ and $\Delta_{2\perp}$, respectively.⁷

TABLE V. Uncertainty estimates for the two-layer structural parameters and V_0 for CuCl(110).

	ω_1	ω ₂	$c_2 - a_1$	$c_1 - a_1$	$c_1 - a_2$	V_0
σ	1.3°	0.4°	0.01 Å	0.01 Å	0.02 Å	0.2 eV

The structure, analysis proceeds by first minimizing the normalized Gaussian R factor^{12,34}

$$R'_{2} = (FI^{2}_{av})^{-1} \sum_{hk} \sum_{i} [cI^{\text{theory}}_{hk}(E_{i}) - I^{\text{expt}}_{hk}(E_{i})]^{2},$$
 (2a)

$$F = n - p - 1, \tag{2b}$$

$$c = N/D, \qquad (2c)$$

$$N = \sum_{hk} \sum_{i} [I_{hk}^{\text{theory}}(E_i)] [I_{hk}^{\text{expt}}(E_i)], \qquad (2d)$$



FIG. 5. Comparison of intensities calculated for the best twolayer relaxation with a Slater exchange parameter X_a of 0.6 [top curve, (a)], best two-layer relaxation with a Slater exchange parameter X_a of 1.0 [second curve from the top, (b)], best single-layer relaxation X_a [third curve from the top, (c)] and the unrelaxed geometry (X_a =1.0) [bottom curve (d)] with measured intensities [dotted curves in (a), (b), (c), and (d)] for the strong (01) beam diffracted from CuCl(110) for normally incident electrons.



FIG. 6. Same as Fig. 5 for the moderate intensity (0-1) beam of electrons diffracted from CuCl(110).

$$D = \sum_{hk} \sum_{i} [I_{hk}^{\text{theory}}(E_i)]^2, \qquad (2e)$$

$$I_{\rm av}^2 = n^{-1} \sum_{hk} \sum_i [I_{hk}^{\rm expt}(E_i)]^2, \qquad (2f)$$

$$n = \sum_{hk} n_{hk}, \qquad (2g)$$

as a function of the *p*-independent parameters (structural and nonstructural) that are to be determined by fitting the intensity data. The n_{hk} are the number of data points in the (hk) beam so that *n* is the total number of data points in the sample. (For example, if multiple angles of incidence are



FIG. 7. Same as Fig. 5 for the moderate intensity (10) beam of electrons diffracted from CuCl(110).

used in the data sample, they also would be summed over to get n.) We perform this step via an automated search routine^{18,29} using the downhill simplex method.³⁵ At its completion we obtain an estimate of the best fit structure. In general, this estimate depends both on the starting structure and on the parameters included in the simplex. Consequently, one must verify the identification of a global minimum by using multiple starting structures and parameter sets.

Uncertainties for the various parameters are calculated as a group from the curvature of the R-factor surface in the vicinity of the global minimum using matrix methods that account for correlations among parameter estimation errors. The R-factor curvature matrix is defined as the second-order

TABLE VI. Gaussian and x-ray r factors for CuBr(110) vs structural and nonstructural parameters. The value of V_0 for the unrelaxed case was not optimized. The notation $c_2 - a_1$ indicates the bond length between the cation in the second layer (bilayer if ω_2 is nonzero) and the anion in the first (surface) "bilayer," etc. All bond lengths, Δ 's, and λ_{ee} are in angstroms.

Structure	ω_1 (deg)	$\Delta_{1,\perp}$	ω_2 (deg)	$\Delta_{2,\perp}$	$c_2 - a_1$	$c_1 - a_1$	$c_1 - a_2$	X_{α}	$\langle u^2 \rangle$	V_0 (eV)	λ_{ee}	R'_2	R_x	R_l
Unrelaxed	0.00	0.00	0.00	0.00	2.464	2.464	2.464	1.0	0.0178	10.00	8	0.50	0.37	0.09
"Best" one-layer relaxation	42.20	0.75	0.00	0.00	2.473	2.304	2.254	1.0	0.0178	13.36	8	0.34	0.35	0.03
"Best" two-layer relaxation with $X_{\alpha} = 1.0$	33.50	0.81	-4.66	0.11	2.533	2.492	1.976	1.0	0.0300	12.36	11	0.29	0.35	0.02
"Best" two-layer relaxation with $X_{\alpha} = 0.6$	36.31	0.76	-4.50	0.11	2.409	2.389	2.294	0.6	0.0300	10.63	11	0.15	0.22	0.01

$$R_{2}'(\mathbf{a}) = R_{20}' + (\mathbf{a} - \mathbf{a}_{est})^{t} \left[\frac{1}{2} \frac{\partial^{2} R_{2}'}{\partial \mathbf{a}^{2}} \right]_{0} (\mathbf{a} - \mathbf{a}_{est}), \qquad (3a)$$

$$(\mathbf{a} - \mathbf{a}_{est})^t = [(\mathbf{a}_1 - \mathbf{a}_1 \text{ est}), \dots, (\mathbf{a}_p - \mathbf{a}_{p,est})].$$
 (3b)

 R'_{20} is the minimum value of R'_2 at the global minimum defined by

$$\mathbf{a}_{\text{est}} = [(a_{1,\text{est}}), \dots, (a_{p,\text{est}})] \tag{3c}$$

in which the a_i must include the independent structural parameters but also may include nonstructural parameters as well (typically V_0 , but also λ_{ee} , $\langle u^2 \rangle$, and X_{α} if desired). The variances σ_i^2 in the (Gaussian) distributions of model parameters caused by uncorrelated, Gaussian distributed errors in the individual intensity values $\{I_{hk}(E_i)\}$ are given by the diagonal terms of the covariance matrix:

$$[\operatorname{cov}\mathbf{a}] = \frac{2R'_{20}}{F} \left[\frac{\partial^2 R'_2}{\partial^2 \mathbf{a}} \right]_0^{-1},$$
(4a)

$$[\operatorname{cov} \mathbf{a}]_{ii} = \sigma_i^2. \tag{4b}$$

These diagonal terms describe the total variance associated with all the variables in the *p*-dimensional vector \mathbf{a} , and hence they tend to increase as more parameters are included in \mathbf{a} . For example, inclusion of the nonstructural parameters increases the variances associated with the structural parameters in those cases in which the two are correlated (provided, of course, uncorrelated random noise in the measurements is the only source of error). These correlations are assessed by examining the correlation matrix

$$P_{ij} = [\operatorname{cov} \mathbf{a}]_{ij} / \sigma_i \sigma_j.$$
 (5)

In the case of fitting experimental data the inclusion of more nonstructural parameters in \mathbf{a} may or may not increase the variances of the structural parameters depending upon whether the residual errors are due primarily to measurement errors or to systematic errors in the model.

We performed the error analysis numerically by fitting a quadratic form [similar to Eq. (3a) but including a nonzero gradient term] to the $R'_2(\mathbf{a})$ surface in the vicinity of the value \mathbf{a}_{est} , located by the simplex search. This code is described by Duke *et al.*¹² Once this form is determined, an improved value of \mathbf{a}_{est} is obtained from its minimum and the

TABLE VII. Effect of nonstructural parameters on the Gaussian r factor for a CuBr(110) structure proposed by Lessor *et al.* (Ref. 36). This was the starting structure for the subsequent two-layer relaxations.

$\overline{X_{\alpha}}$	$\langle u^2 \rangle$	V_i	λ_{ee}	R'_2
1.0	0.0300	3.78	0	0.43
0.6	0.0300	3.78	0	0.25
0.6	0.0178	3.28	0	0.37
0.6	0.0178	0	11	0.21
0.6	0.0300	0	11	0.18

associated elements of the curvature matrix $[\partial^2 R'_2 / \partial \mathbf{a}^2]_0$ in Eq. (3a) are determined. Inversion of the curvature matrix yields the covariance matrix, Eqs. (4), which is converted to the correlation matrix using Eq. (5).

IV. RESULTS

A. CuCl(110)

The starting point of our structural search for CuCl(110)was the single-layer ($\omega_2=0$) "best fit" structure reported earlier⁶ obtained using a manual process to minimize the x-ray R factor, R_x . We performed a search for an improved optimal structure, using R'_2 rather than R_x as the function to be optimized and a five-variable simplex defined by ω_1, V_0 , and the three bond lengths connecting the surface atoms to their neighbors. At the completion of this simplex we fit the $R'_{2}(\mathbf{a})$ surface to a quadratic form to obtain an improved estimate of the five parameters, and an assessment of their uncertainties. All of these fitting calculations were performed using rigid-lattice phase shifts and treating the scattering from the first four layers exactly. When we had obtained the "best one-layer relaxation" in this way, we recalculated the theoretical intensities using the $\langle u^2 \rangle$ discussed in Sec. III A and treating scattering from the first six layers exactly to achieve a completely converged model calculation. The Rfactors were recalculated using these intensities. They are given in the third row of Table I in which they are compared with the results for the unrelaxed and prior best-fit structures.⁶ It is evident from this table that our automated software gives results close to those obtained previously by a manual search⁶ for a single layer relaxation. The inclusion of ω_2 into the search procedure (to generate a six-variable optimization) leads to large increases in ω_1 , however, because ω_1 and ω_2 are both strongly correlated with other structural

TABLE VIII. Covariance matrix for the "best" two-layer relaxation of CuBr(110) specified in row 4 of Table VI. The diagonal elements are an estimate of σ^2 for the labeled parameter.

	ω_1	ω_2	$c_2 - a_1$	$c_1 - a_1$	$c_1 - a_2$	V_0
$\overline{\omega_1}$	1.676×10^{-1}	1.153×10^{-2}	7.897×10^{-4}	-2.071×10^{-3}	2.592×10^{-3}	5.518×10^{-3}
ω_2	1.153×10^{-2}	5.002×10^{-2}	-2.451×10^{-4}	1.199×10^{-4}	6.130×10^{-5}	1.973×10^{-3}
$c_2 - a_1$	7.897×10^{-4}	-2.451×10^{-4}	4.994×10^{-5}	-1.038×10^{-5}	-2.151×10^{-5}	-1.923×10^{-4}
$c_1 - a_1$	-2.071×10^{-3}	1.199×10^{-4}	-1.038×10^{-5}	4.817×10^{-4}	-5.097×10^{-5}	-1.415×10^{-4}
$c_1 - a_2$	2.592×10^{-3}	6.130×10^{-5}	-2.151×10^{-5}	-5.097×10^{-5}	1.194×10^{-4}	-1.494×10^{-5}
V ₀	5.518×10^{-3}	1.973×10^{-3}	-1.923×10^{-4}	-1.415×10^{-4}	-1.494×10^{-5}	8.675×10^{-3}

 $c_1 - a_1$ V_0 ω_1 ω_{2} $c_2 - a_1$ $c_1 - a_2$ 1.259×10^{-1} 2.730×10^{-1} -7.289×10^{-1} 1.447×10^{-1} 5.794×10^{-1} 1 ω_1 7.722×10^{-2} 2.509×10^{-2} 1 -1.551×10^{-1} 9.474×10^{-2} ω_2 -2.115×10^{-1} -2.785×10^{-1} 2.922×10^{-1} 1 $c_2 - a_1$ 2.189×10^{-1} -6.721×10^{-1} $c_1 - a_1$ -1.468×10^{-2} 1 $c_1 - a_2$ 1 V_0

TABLE IX. Correlation matrix corresponding to the covariance matrix in Table VIII.

variables, as evident upon comparing rows three and four of Table I. The results of the full six-variable optimization are given in row four of Table I.

To our surprise, however, the structure specified by row four of Table I is not identical to a previously published⁷ multilayer best fit for CuCl(110) in which R_x , rather than R'_{2} , was used as the figure of merit to be minimized. The differences are quite discernable: even the signs of the deviations of $c_2 - a_1$ and $c_1 - a_2$ from their bulk values are inverted. After considerable detective work, this result was found to be primarily a consequence of the use of different values of X_{α} in the atomic potential: $X_{\alpha}=1$ by us versus $X_{\alpha} = 0.7$ by Lessor *et al.*⁷ This discovery led us to analyze the effect of nonstructural parameters on the quality of the fit of the structure of Lessor et al. to the LEED intensity data. The results of this study are summarized in Table II. The minimum value of R'_2 is obtained for $X_{\alpha}=0.6$, using the other nonstructural parameters used by Lessor et al. (i.e., $-\ln\Sigma = V_i = 4.2$ eV). This change alone reduces R'_2 by 31%, with only small subsequent improvements induced by varying Im Σ and $\langle u^2 \rangle$. Using "historical" values^{11,19} for the nonstructural parameters, the structure of Lessor et al.⁷ gives a significantly poorer ($R'_2 = 0.26$ versus $R'_2 = 0.16$) fit to the measured intensities than the best-fit structure specified in row four of Table I.

Using the revised "best fit" nonstructural parameters in a complete new six-parameter structural search starting from the Lessor *et al.*⁷ structure leads to the best-two-layer relaxation specified in row 5 of Table I. This structure is substantially the same as that of Lessor *et al.*⁷ with $c_2 - a_1$ being contracted from its bulk value and $c_1 - a_2$ being expanded. The covariance and correlation matrices for this structure are given in Tables III and IV, respectively, with the resulting uncertainty estimates being collected in Table V. The quality of the fits to the measured LEED intensities is shown in Figs. 5–7 for the three lowest-order beams, i.e., (01), (0-1), and (10), respectively. Results for the unrelaxed (top row, Table I) and best-single-layer (third row, Table I) are included in Figs. 5–7 so that the reader can assess the visible significance of the improvements in R'_2 quoted in Table I. The intrinsic reproducibility of the intensity data themselves is $R'_{2.\text{expt}} = 0.08$ estimated by comparing the two data sets,

TABLE X. Uncertainty estimates for the two-layer structural parameters and V_0 for CuBr(110).

	ω_1	ω_2	$c_2 - a_1$	$c_1 - a_1$	$c_1 - a_2$	V_0
σ	0.4°	0.2°	0.01 Å	0.01 Å	0.01 Å	0.1 eV

which were averaged to give the "experimental" curves for CuCl(110). Thus, even for optimized nonstructural parameters, roughly half the residual uncertainty R'_{20} is due to uncertainties associated with the definition of the LEED multiple scattering model as opposed to those associated with the reproducibility of the experimental measurements.

B. CuBr(110)

A procedure essentially identical to that used for CuCl(110) was employed to obtain the optimal estimates for the CuBr(110) surface structural parameters and the errors therein. Our starting structure for the initial simplex search for the best single-layer relaxation was that previously obtained⁶ for CuCl(110) scaled by the difference in the bulk lattice parameter. We estimated $\langle u^2 \rangle_{Cu} = \langle u^2 \rangle_{Br} = 0.017 \text{ Å}^2$ as described in Sec. III A, for a fixed value of $\lambda_{ee} = 8 \text{ Å}$ as in the case of CuCl. A five-parameter (ω_1 , V_0 , and three surface bond lengths) simplex search when refined by the quadratic fit to the R'_2 surface gives the "best one-layer relaxation"



FIG. 8. Same as Fig. 6 for CuBr(110).



FIG. 9. Same as Fig. 5 for CuBr(110).

structure specified in Table VI, associated with nonstructural parameters characteristic of prior work on CuCl.

For CuBr(110), we had an unpublished structure,³⁶ analogous to the CuCl(110) structure of Lessor et al.,7 resulting from a gradient-method search using R_x as the figure of merit and a value of $X_{\alpha} = 0.7$ rather than 1.0 in the construction of the atomic potential. Thus, we repeated the CuCl(110) study of the effect of the nonstructural parameters on the value of R'_2 for this structure for CuBr(110) with the results given in Table VII. Again we found a best fit for $X_{\alpha} = 0.6$ resulting in a major improvement in R'_{2} together with much smaller improvements associated with optimizing $\langle u^2 \rangle$ and λ_{ee} (or V_i). Thus, the nonstructural parameters given in the bottom row of Table VII were selected to use in the search to determine the optimum structure of CuBr(110). The results obtained thereby are shown in the fourth row of Table VI whereas those obtained using $X_{\alpha} = 1$ are given in the third row of Table VI. As in the case of CuCl(110) we find significant changes in the bond lengths emanating from the two analyses. For CuBr(110) these differences call into question the contraction of the backbond in the top layer as evident from comparison of rows three and four of Table VI.

The two-layer, optimal structure for CuBr(110), obtained using the best-fit nonstructural parameters, is given in row four of Table VI. The resulting covariance and correlation matrices are presented in Tables VIII and IX, respectively. The parameter uncertainty estimates resulting from measurement uncertainties are indicated in Table X. The reproducibility of the data, as measured by comparison of the two data sets averaged to obtain the experimental LEED intensities used in the analysis, is $R'_{2,expt}$ =0.04, twice as good as for



FIG. 10. Same as Fig. 7 for CuBr(110).

CuCl(110). The quality of the fits to these intensities is about the same as for CuCl(110) as evident from the descriptions of the (0-1), (01), and (10) beams evident in Figs. 8–10, respectively. In contrast to CuCl(110), the extension of the analysis to include two versus one layer relaxations and the use of lower values of X_{α} makes a decisive improvement in the visual quality of the fits. Nevertheless, model uncertainty rather than data uncertainty accounts for over 70% of the residual values R'_{20} .

V. DISCUSSION

The main consequences of our structure analyses reported in Tables I and VI are that relaxations of the (110) surfaces of CuCl and CuBr penetrate to the second layer, that the surface cation-anion bond in CuCl and the surface cation back bond in CuBr are contracted by amounts larger than the uncertainties in the analysis, and that changes in the other bond lengths are smaller and are sensitive to the model of the exchange interaction used in constructing the atomic potential. The contractions of the surface bond length may correlate with ionicity as proposed earlier,^{7,37} but changes in the back bonds seem to be too sensitive to the construction of models of the electron-solid interaction to be extracted meaningfully from the analysis, with the possible exception of the surface cation backbond contraction for CuBr(110).

The use of rigorous statistically based uncertainty analysis³⁴ allows us to make quantitative statements about the precision and accuracy of our results. For a given model electron-solid interaction, all of the surface bond length changes lie outside the 68% confidence levels, $\pm \sigma$ from



FIG. 11. Schematic indication of the parameters used to convert bond angles and lengths into the structural parameters used in the input files for the LEED intensity calculations.

Tables V and X from the bulk values, and hence within the precision³⁸ of our analysis. Unfortunately we cannot assert that they lie within the accuracy of the analysis,³⁸ because values of R'_2 corresponding to comparisons of different data sets are less than the minimum values given in Tables I and VI. Systematic errors associated with the construction of the model rather than data reproducibility are expected to limit the quality of the best fits specified in the tables. This is a common situation in LEED intensity analyses.³⁹ We developed in detail a graphic example of this result by exploring the sensitivity of the predicted optimum structures on the values of X_{α} used in constructing the atomic potential. Changes in the optimum bond lengths for CuCl(110) are 0.06 Å for $c_2 - a_1$, 0.03 Å for $c_1 - a_1$, and 0.21 Å for $c_1 - a_2$, all far larger than the statistical uncertainties of 0.01 Å for $c_2 - a_1$, $c_1 - a_1$, and 0.02 Å for $c_1 - a_2$ given in Table V. For CuBr(110) they are 0.12 Å for $c_2 - a_1$, 0.1 Å for $c_1 - a_1$, and 0.31 Å for $c_1 - a_2$, also far larger than the values given in Table X. The possibility of such results is signaled in our uncertainty analysis by the fact that the residuals for fitting the data by the optimal model, $R'_{20}(CuCl) = 0.14$ and $R'_{20}(CuBr) = 0.15$, are two to three times larger than those associated with the reproducibility of the data sets, $R'_{2.expt}(CuCl) = 0.08$ and $R'_{2.expt}(CuBr) = 0.04$. Thus, our quantitative statistical analysis provides an indication that model uncertainties associated with nonstructural parameters (especially those associated with the construction of the electron-ion-core phase shifts) can overwhelm structural parameter uncertainties associated with data measurement uncertainties. This is not a new conclusion, but our quantitative analysis of these uncertainties permits us to assess their magnitude for specific structural parameters.

Finally, our analysis convinced us of the necessity of using an adequate number of structural variables in a complete simultaneous optimization. In this case ω_1 and ω_2 are both strongly correlated with the other structural variables leading to the optimal values of ω_1 changing substantially (by as much as 6°) when ω_2 is included in the analysis. This is reflected in the shape of the R'_2 surface. In these cases an accurate fit of the shape of this surface in the final step of the analysis [Eqs. (3) and (4)] is required to give a positive definite curvature matrix. Moreover, the positive definiteness of the curvature matrix is a good indicator that a local minimum has been found. In many cases the outcome of the simplex search, while apparently converged, was not sufficiently close to the minimum to meet the criterion of positive definite curvature, suggesting that search procedures that do not explicitly determine the shape of the $R'_2(\mathbf{a})$ surface in the vicinity of the chosen structure can give misleading estimates of the structure. Use of enough variables and an explicit test for a local minimum proved to be important factors in estimating the structural parameters from the experimental data sets.

VI. SYNOPSIS

In this paper we report sets of low-temperature normal incidence LEED intensity data for CuCl(110) and CuBr(110) and analyze these data using a new statistically based, multidimensional uncertainty analysis procedure. This analysis permits us to extract estimates of highly correlated physically based surface structure parameters (i.e., tilt angles and bond lengths, as shown in Fig. 3) within statistically significant confidence intervals on the basis of the *a priori* assumption that the uncertainties in the experimental LEED intensities limit those in the resulting structural parameters. On this basis, we demonstrate that for the highly ionic CuCl and CuBr zinc-blende(110) surfaces, small surface bond-length changes occur. These changes are compatible with the results of prior analyses^{6,7} of the CuCl(110), with the understanding of the dependence of the structure of zinc-blende (110) surfaces on the ionicity of the bulk chemical bonding afforded by currently available local density functional calculations,⁸ and with trends expected in the dependence of the surface structures of zinc-blende (110) semiconductors on ionicity as well as atomic size.^{7,37} The large effect of the model of the exchange interaction on the optimal surface structural parameters extracted from LEED is unexpected, however, and merits further examination.

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APPENDIX A: GENERATION OF TRIAL SURFACE STRUCTURES

In order to use any of the "automated" search routines, we need to convert the bond lengths and angles of a given step into a LEED input file suitable for our dynamical LEED routine. This was accomplished by adapting subroutines obtained from Lessor at Pacific Northwest Laboratories. In Fig. 11, we show some of the parameters necessary for this mapping.

The routines take as input the bond lengths (labeled a_1, b_1, c_1, a_2 , etc.) and the shear in the layer of interest (labeled $b_{2,z}$) and in the layer beneath (called $b_{1,z}$). In the figure, $b_{2',z}$ is $b_{2,z}$ for the surface layer and was called $\Delta_{1,\perp}$ in our earlier papers.

In a bulk layer, all parameters are known. In the first reconstructed layer above the bulk, the only unknowns are the y and z components of a_2 and c_2 . These can be determined by solution of the following four simultaneous quadratic equations from which the correct roots can be extracted:

$$a_{2,y} = \sqrt{(a_2)^2 - (a_{2,x})^2 - (a_{2,z})^2},$$

$$a_{2,z} = -(b_{1,z} + b_{2,z} + c_{2,z}),$$

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$$c_{2,y} = a_0 - (a_{2,y} + b_{1,y} + b_{2,y}),$$

$$c_{2,z} = \sqrt{(c_2)^2 - (c_{2,y})^2 - (c_{2,y})^2}.$$

The same is true for any remaining layers above that. The z component of b_2 (shear) can be determined from the angles as shown in Fig. 2 of the text. The bond length, b_2 , is given, and $b_{2,x}$ (and $b_{1,x}$) is always $a_0/8^{1/2}$ (i.e., they are fixed by symmetry for the zinc-blende lattice). Since b_2 , $b_{2,x}$ and $b_{2,z}$ are known, $b_{2,y}$ may be calculated from a single quadratic:

$$b_{2,y} = \sqrt{(b_2)^2 - (b_{2,x})^2 - (b_{2,z})^2}.$$

The x components of a and c are always zero.

These routines return the vectors labeled **1** through **7** in Fig. 11 (and more, if additional layers are reconstructed). Proper addition or subtraction of the components of the real lattice vectors $a_{0,x}$ and $a_{0,y}$ to these values yield the interatomic vectors used in our LEED routine.

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