Anisotropic Atomic Motions in Structural Analysis by Low Energy Electron Diffraction

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(Received 21 August 1992)

The structure of the $\sqrt{3}\times\sqrt{3}R30°$ overlayer formed by CO molecules adsorbed on a Ru(0001) was analyzed by low energy electron diffraction. Anisotropic atomic motions under the influence of thermal excitation were taken into account by adopting the concept of split positions. Apart from considerable improvement in the structural refinement this technique provides information about dynamic processes. In particular, the molecular axis of the CO molecules was found to be tilted on the average by $(12\pm3)°$ at 150 K, which is attributed to excitation of the bending mode vibration (i.e., frustrated translation).

PACS numbers: 68.35.Bs, 61.14.Hg, 68.45.Da

The influence of thermal vibrations at surfaces on the intensities in low energy electron diffraction (LEED) has long been recognized [1,2], but so far its impact on structural analysis has found only little attention. Usually the concept of an effective Debye-Waller factor characterized by a Debye temperature θ is introduced as a correction to relate the scattering amplitudes with thermal vibrations [3,4]. If one assumes isotropic and uncorrelated displacements of the atoms, this concept leads to temperature-dependent phase shifts for the scattering of electrons in the multiple-scattering theory. In LEED structural analysis the Debye temperature θ (which usually depends markedly on energy) may be treated as an additional fit parameter or is even kept constant. This approach works remarkably well in the LEED structural analysis of clean surfaces or simple adsorbate systems as demonstrated with numerous systems [5]. However, it is certainly a strong oversimplification since vibrations at surfaces are definitely anisotropic, in particular if these are adsorbate covered, and hence the several examples that exist in the literature with relatively poor agreement between experimental and calculated LEED intensity-voltage curves (as quantified by the resulting r factors) most likely have to be attributed to such an effect [6,7]. This conclusion is supported by comparison with x-ray structure analysis where low r factors and high accuracy of the structural data can only be reached by introduction of anisotropic or even anharmonic vibrations. For surface-sensitive diffraction techniques with dominant single-scattering events these effects have been partly involved [8–10].

The first approach to take account of the influence of anisotropic vibrations on the LEED intensities was to multiply the layer scattering matrices with anisotropic temperature factors [11]. Further attempts to include anisotropic vibrations in intralayer multiple scattering were made by renormalization of the single-site scattering t matrix via an anisotropic Debye-Waller factor [12]. The applicability of this approach has not yet been sufficiently investigated.

It is evident that proper inclusion of anisotropic temperature effects in the calculations of LEED intensities would improve the quality of structural refinements. Moreover, this approach might even provide additional information on the *dynamics* beyond that on *static* structural properties, through evaluation of the probability density function (PDF) which can be derived from the Fourier transform of the temperature factor [13]. This idea was recently advocated by Pendry [14] in connection with the analysis of diffuse low energy electron diffraction (DLEED) experiments. He suggested that derivation of the probability distribution of adsorbed particles around their adsorption site would provide information about those of their motions which exhibit the largest amplitudes, and hence lowest excitation energies, usually not so easily accessible with conventional techniques of vibrational spectroscopy.

The present paper reports on the first successful attempt to verify both aspects of the outlined ideas by using the system CO/Ru(0001)-$\sqrt{3}\times\sqrt{3}R30°$ as a test case. This system had already previously been the subject of a conventional LEED structural analysis [7]. There it was found that the CO molecules are adsorbed through their carbon atoms over single Ru atoms (i.e., in "on-top" positions) with the molecular axis being parallel to the surface normal. This general conclusion was confirmed by additional techniques such as angle-resolved ultraviolet photoelectron spectroscopy (ARUPS) [15] and electron stimulated ion angular distribution (ESDIAD) [12], but the agreement between experimental and theoretical LEED intensity data was rather unsatisfactory as reflected by an optimum Pendry r factor of $r_P=0.51$. The situation was even worse for the fractional-order beams which are most sensitive to the actual structure of the adsorbate; for example, for the $(\frac{7}{3},\frac{2}{3})$ beam only $r_P=0.8$ was reached. One possible reason for this discrepancy might be the neglect of effects of surface relaxation in this early work, and therefore at first the original experimental intensity-voltage (I-V) data recorded at 150 K [7] were subject to a more refined (but still conventional) theoretical analysis by including the possibility for horizontal and vertical displacements of the substrate atoms. Details about the experiment and the phase shifts used can be found in Ref. [7].

In the present analysis an extended version of refinement of structural parameters [16] was used. The agreement between experimental and theoretical I-V data was quantified by both the r_{DE} factor [17] to which the optimization scheme is adopted and Pendry's r_P factor [18]. Our analysis clearly confirmed the on-top site of adsorbed CO. However, the Ru atoms coordinated with CO were found to be displaced outwards by 0.07 ± 0.03 Å which is associated with a significant decrease of both r factors: The r_{DE} factor drops from 0.44 to 0.32 and Pendry's r_P factor shows a pronounced decrease from 0.51 to 0.34.

The resulting "static" structure with the associated parameters is displayed in Fig. 1. The Ru-C (1.93 ± 0.04 Å) and C-O (1.10 ± 0.05 Å) distances are within the expected ranges.

The approach to simulate the distribution functions $n_i(R_i)$ of the atoms constituting the atoms of the adsorbate was adopted from x-ray crystallography [13]: The scattering of both x rays and electrons occurs on a much faster time scale than the nuclear motion. To a first approximation it is hence reasonable to locate the atoms in those positions which are most frequently occupied during their thermal motions. These will deviate from the equilibrium positions by amounts $\pm \Delta R_i$ (split positions). "Split positions" means that the atom is statistically distributed over two or more symmetrically equivalent sites. This approximation is well established in x-ray crystallography. Within the kinematic theory anisotropic vibrations and split positions are indistinguishable if the magnitude of splitting is much smaller than the atomic diameter. For LEED, as the simplest approach, partially occupied sites can be introduced in the multiple scattering formalism of the average t-matrix approximation (ATA) [19]. For both the C and O atoms displacements along the surface normal, $\Delta R_{\mathrm{C},\perp}$, and $\Delta R_{\mathrm{O},\perp}$, respectively (reflecting the M-CO vibration), as well as parallel to the surface, $\Delta R_{\mathrm{C},\parallel}$ and $\Delta R_{\mathrm{O},\parallel}$, respectively (corresponding to the "wagging" mode of vibration of the molecular axis) were taken into account.

Optimal structural refinement was found for vertical displacements of the C and O atoms of $\Delta R_{\mathrm{C},\perp} = 0.04$ Å and $\Delta R_{\mathrm{O},\perp} = 0.03$ Å, respectively, and for lateral displacement of the C atom of $\Delta R_{\mathrm{C},\parallel} = 0.04$ Å. These numbers are equivalent to an (isotropic) effective Debye temperature of $\theta = 400$ K. However, quite different and much more pronounced effects were found for $\Delta R_{\mathrm{O},\parallel}$, as expected. Here various azimuthal orientations of the displacements were taken into consideration: Split positions corresponding to retention of the local $p3ml$ symmetry of the adsorbed CO molecule are depicted in Fig. 2. Alternatively, motions along the $[11\bar{2}0]$ orientation towards the "bridge" positions might take place, and finally not only 3 but 6 equivalent positions would have to be taken into account. There was no significant difference in the results for the various geometries, so that we have to conclude either that the applied procedure is not sensitive enough to discriminate between various types of azimuthal orientations of the displacements for the O atoms or that the latter are in fact highly isotropic. The discussion of the calculation procedure will hence be exemplified with the situation illustrated by Fig. 2.

In the LEED intensity calculations all multiple scattering paths between the split positions were suppressed. The three positions of the O atom were occupied with equal probabilities. During calculation of the lattice sum all contributions arising from interatomic distances < 0.8 Å were ignored. This approach is denoted as lattice sum (LS) mixing. It corresponds to the ATA with zero scattering at one site. A detailed description of the formalism will be given elsewhere [20]. An alternate way (amplitude mixing) consists in calculating the amplitude for one split position (reducing the threefold symmetry to

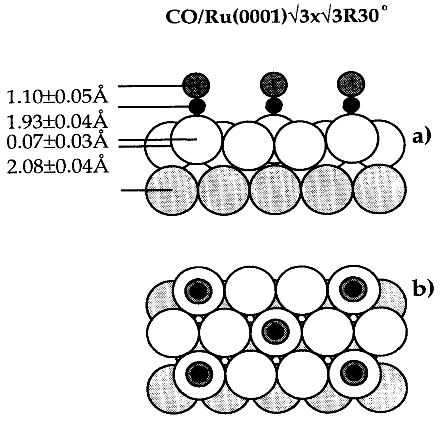

FIG. 1. Structure model for the CO/Ru(0001)-$\sqrt{3}\times\sqrt{3}R30°$ phase. Small shaded circles: O atoms; small filled circles: C atoms. (a) Side view; (b) top view. The corresponding r factors are $r_P = 0.29$ and $r_{\mathrm{DE}} = 0.26$.

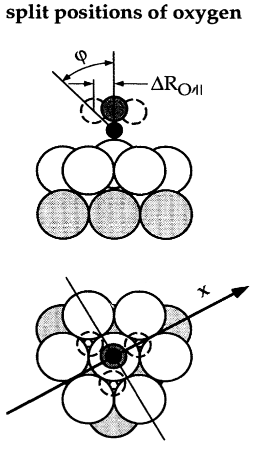

FIG. 2. Illustration of O split positions which are compatible with the threefold symmetry. The oxygen atom is shifted along the line x by an amount $\Delta R_{\mathrm{O},\parallel}$ (split position); the two other split positions are generated by operation of the threefold rotational axis.

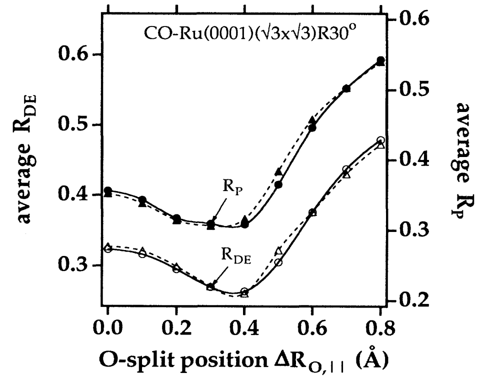

FIG. 3. Overall r factors r_P (filled symbols) and r_{DE} (open symbols) as a function of the split position $\Delta R_{\mathrm{O},\parallel}$ using LS mixing (dashed line) and amplitude mixing (full line).

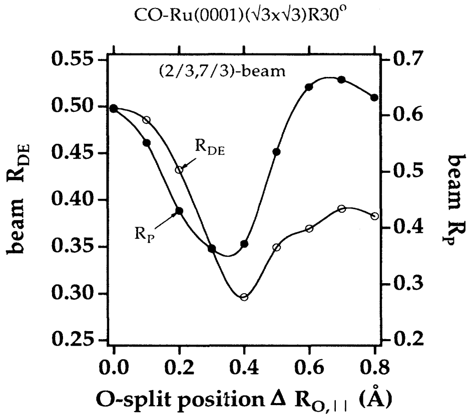

FIG. 4. r_P and r_{DE} for beam $(\frac{7}{3},\frac{2}{3})$ as a function of the O split position $\Delta R_{\mathrm{O},\parallel}$.

a mirror plane) and in performing a coherent mixing of the amplitudes with respect to the local (threefold) symmetry. Subsequently the resulting amplitudes have to be mixed incoherently with regard to the symmetry of the experimental pattern (6 mm). It turned out that both approaches led to almost identical results (see Fig. 3), which becomes plausible if one considers that multiple scattering effects within the CO layer are only weak. However, the LS procedure required only about half of the computational effort thanks to its higher symmetry properties.

Figure 3 displays the variations of the overall r factors (r_P and r_{DE}) with $\Delta R_{\mathrm{O},\parallel}$, starting with the optimal "static" structure as presented above, by applying both outlined approaches. Evidently both the LS mixing and the amplitude mixing procedures lead to almost identical results. Both r factors reach a minimum ($r_P=0.29$ and $r_{\mathrm{DE}}=0.26$) for $\Delta R_{\mathrm{O},\parallel}=0.4$ Å, with an uncertainty of ± 0.15 Å as derived from the curvature of the plot. Obviously, r_{DE} reacts somewhat more sensitively than r_P, which is plausible in view of the different definitions of these r factors: The vibrational amplitudes affect the relative intensities of I-V peaks more than their energetic positions.

More detailed inspection of the r factors for individual beams yields that integral order beams are nearly unaffected by these effects, while fractional order beams—and in particular those with large momentum transfer parallel to the surface—react very sensitively. For the $(\frac{7}{3},\frac{2}{3})$ beam, for example, the r_P factor already decreased from 0.8 to 0.5 by allowing for vertical relaxation of the Ru atoms forming the adsorption sites, but drops even to $r_P=0.34$ (and r_{DE} from 0.5 to 0.29) if $\Delta R_{\mathrm{O},\parallel}$ is varied from 0.0 to 0.4 Å (Fig. 4). The improvement of the structural refinement becomes evident also from visual inspection by comparing the experimental I-V curves with those calculated for varying lateral displacements $\Delta R_{\mathrm{O},\parallel}$, as reproduced in Fig. 5. In particular, for energies >200 eV both the peak positions and intensities vary with alteration of $\Delta R_{\mathrm{O},\parallel}$ and achieve better agreement with the experimental data.

One might now wonder if the static structure parameters derived previously by taking into account an isotropic correction in terms of a Debye temperature might be affected by inclusion of the dynamic effects as modeled by the introduction of split positions. Therefore another automatic structural refinement with inclusion of the split position parameters was performed. The resulting optimum structure agreed within the error bars with that

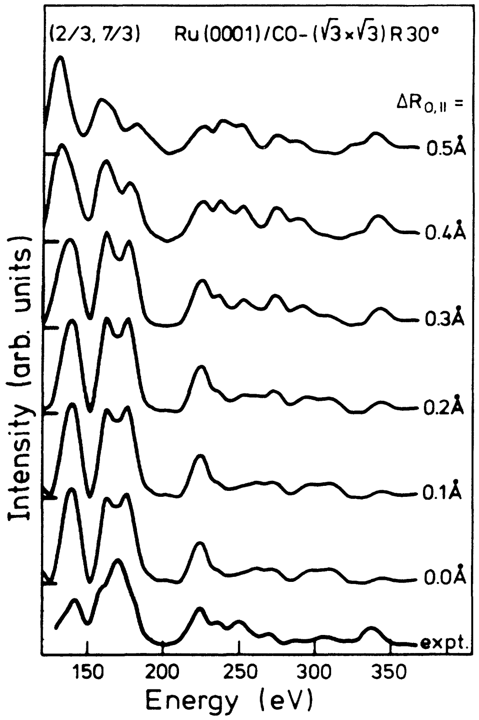

FIG. 5. Comparison of experimental data [$(\frac{7}{3},\frac{2}{3})$ beam] and calculated I-V curves for varying split positions $\Delta R_{\mathrm{O},\parallel}$.

quoted above as derived with an (isotropic) Debye temperature. However, the r factor minima are deeper, as outlined, and hence render much more reliability to the accuracy of the structure determination.

The second, and probably even more important, conclusion concerns the possibility to extract information about *dynamic* processes on surfaces from analysis of low energy electron diffraction data.

The findings that (at 150 K) the average lateral displacement of the O atom amounts to 0.4 Å and is 1 order of magnitude larger than that of the C atom (0.04 Å) is equivalent to a mean inclination of the molecular axis φ by $(12\pm3)^\circ$ with respect to the surface normal (cf. Fig. 2). This conclusion is in nice agreement with the results of an ESDIAD study for the same system [21]. There it was found that the patterns created by the trajectories of desorbing species are centered around the surface normal with their widths being temperature dependent. More specifically, the half angles at half maximum of the ion cones (reflecting the average inclination of the molecular axis of the adsorbed CO molecules) were derived to be about 16° at 290 K and 12° at 90 K without any detectable azimuthal anisotropy.

These effects have to be attributed to thermal excitations of the bending mode vibration (i.e., frustrated translation) of the adsorbed CO molecules. For the CO/Pt(111) system which forms likewise a $\sqrt{3}\times\sqrt{3}R30^\circ$ overlayer structure with the CO molecules in on-top positions. Schweizer *et al.* [22] estimated from *IR* data that the potential for tilting a CO molecule towards the bridge site is rather flat and decreases by only about 30 meV for a displacement $\Delta R_{\mathrm{O},\parallel}$ of 0.5 Å, giving rise to a rather small excitation energy of the corresponding vibration. The latter was indeed determined experimentally for the CO/Pt(111) system by means of inelastic He atom scattering to be about 6 meV [23]. If this value is compared with the thermal energy at 150 K (15 meV), it becomes evident that this bending vibration will be markedly excited. Anharmonic effects will lead to a further increase of the populations of higher quantum levels and thus enhance the mean square amplitude. The much lower value found for the lateral displacement of the C atom ($\Delta R_{\mathrm{C},\parallel}=0.04$ Å) supports the identification of this motion with a bending mode vibration in which the C atom is essentially kept fixed. The lowest-lying excitation for a motion perpendicular to the surface is the M-CO vibration with an energy of 55 meV [24] in which the whole CO molecule vibrates against the surface. In this case the population of excited states will be very low at 150 K, and accordingly the values for $\Delta R_{\mathrm{C},\perp}$ and $\Delta R_{\mathrm{O},\perp}$ should be very small in agreement with conclusions of the present analysis.

The temperature dependence of the discussed effects is currently under experimental investigation [25]. Preliminary results show the expected decrease of $\Delta R_{\mathrm{C},\parallel}$ with decreasing temperature.

The authors are grateful to D. Menzel for providing the experimental LEED I-V data, and to H. Bludau, M. Gierer, and T. Hertel for stimulating discussions.

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