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Tensor LEED study of the temperature dependent dynamics of the NaCl(100) single crystal surface

Jochen Vogt*

Chemisches Institut der Otto-von-Guericke Universität Magdeburg, Universitätsplatz 2, 39106 Magdeburg, Germany

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The structure and dynamics of the NaCl(100) single crystal surface were investigated at 25, 100, 160, and 230 K by means of low-energy electron diffraction (LEED). At each temperature, diffraction peak intensities of four inequivalent beam orders were recorded as a function of electron energy. The experimental $I(V)$ data were analyzed using the tensor LEED approach. Compared to the unrelaxed bulk geometry, the Na^+ ions in the topmost layer are displaced inwards by 0.09 ± 0.03 Å at all investigated temperatures. Moreover, the root-mean-square vibrational amplitudes of Na^+ and Cl^- ions in the topmost layer are enhanced significantly in the investigated temperature range. The amplitudes of the ions in the second layer are close to the bulk values. While the amplitudes of the cations in the second layer are larger than those of the anions, Na^+ and Cl^- in the topmost layer have nearly equal vibrational amplitudes at temperatures above 100 K. In this temperature range, the mean-square amplitudes of vibrations of ions at the surface and in the bulk are in good agreement with previously reported lattice dynamics studies.

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I. INTRODUCTION

Atom and ion scattering[1–7] studies as well as electron-diffraction experiments,[8,9] performed on ordered surfaces of a wide variety of materials, provide evidence that the vibrational amplitudes of atoms and ions at the interfaces of solids are larger than the respective bulk values.

Some materials have shown unexpectedly high vibrational amplitudes of the atoms at the surface. The latter exceed the bulk values often by a factor of 2 and more.[10]

The equilibrium positions and vibrational amplitudes of atoms or ions near a solid's surface may provide information about the forces acting on them. Therefore, the structure and dynamics of surfaces have always attracted much theoretical interest. For the material NaCl under study in this work, an accurate knowledge of interionic forces is relevant in many respects, e.g., for the study of melting and wetting,[11–13] the problems of self-trapped excitons near the surface,[14] the simulations of image contrast in atomic force microscopy,[15] or the atomistic simulation of friction.[16]

In many cases, the force constants are derived from bulk properties or, more recently, from *ab initio* calculations.[17] Usually, these potential models are also extended to surface atoms or ions.[18] For surfaces of ionic substrates such as, e.g., NaCl(100), various potential models and *ab initio* studies predict a rumpling of the ions in the first few layers.[14,15,19–21] Detailed element-specific predictions of the surface vibrational amplitudes of ions in the high-temperature range have been made by means of molecular-dynamics simulations based on a rigid-ion potential.[12] Theoretical studies of the surface dynamics at low temperatures were based on rigid-ion, deformation-dipole, and shell-model potentials.[22–24]

Unfortunately, an experimental confirmation of these results by means of low-energy electron diffraction (LEED) was limited for a long time to the measurement of the attenuation of beam intensities as a function of temperature, from which the surface Debye temperature Θ_D can be determined. From the ratio of Θ_D and the bulk Debye temperature, the mean-square amplitudes (MSAs) of the surface ions can be related to those of the bulk ions.[25] This method, however, can only give an average value for the vibrational amplitudes and neglects, moreover, multiple scattering events in electron scattering.[9]

Moreover, although the first LEED experiments on alkali halides were already reported in the pioneering time of surface science,[26,27] LEED experiments with insulator single crystal surfaces at low temperatures were hampered due to charging effects and surface defect generation.

Techniques such as the tensor LEED (TLEED) method[28–30] allow the extraction of much more detailed information about the interface dynamics, namely, an element-specific and layer-resolved determination of vibrational amplitudes of the ions at the interface.[30] Due to the use of channel plates for image intensification,[31] quantitative LEED techniques such as TLEED could be extended even to wide-band-gap insulators such as MgO (Ref. 32) or CaF_2 at temperatures as low as 20 K.[33]

A recent comparative experimental and theoretical study of the dynamics of the $CaF_2(111)$ interface at 300 K gave qualitative agreement between tensor LEED results and molecular-dynamics simulations.[34] The goal of this paper is to report LEED experiments, which were performed with NaCl(100) single crystal surfaces at different temperatures from 25 to 230 K. Structure searches based on the TLEED approach will be presented by means of which the positions and the root-mean-square (rms) vibrational amplitudes of the various ions in the first two layers were fitted to the experimental $I(V)$ data at different temperatures. The results can be directly compared to lattice dynamics or molecular-dynamics calculations and might thus contribute to the improvement or testing of interaction potentials for NaCl.

This paper is organized as follows: In Sec. II, the LEED experiment is briefly described and the obtained data are presented. In Sec. III, the applied tensor LEED method is shortly summarized and the results are reported, which are

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discussed in detail in Sec. IV. The paper ends with a brief summary.

II. EXPERIMENT

The experimental setup used in this study has been described extensively in previous publications.[33–35] Therefore, only the most important details are summarized.

A NaCl single crystal (Korth, Germany) was cleaved in dry nitrogen atmosphere and mounted on a sample holder. The latter was transferred into an ultrahigh-vacuum chamber within 30 min. After bakeout, a pressure of 3×10^{-10} mbar was reached. Under measurement conditions, the base pressure was lower than 1×10^{-10} mbar. The sample holder was connected to a closed-cycle helium refrigerator for sample cooling down to temperatures of 20 K. Temperatures between 20 and 400 K could be set with a stability of 0.1 K by means of an electrical resistance heater. The temperature was measured by means of a silicon diode (LakeShore), which was clamped close to the crystal onto the sample holder.

The LEED experiments were performed by means of a microchannel plate LEED optics (MCPLEED, Omicron). Due to the signal amplification of the MCPLEED, primary electron currents in the nanoampere range are possible and thus LEED experiments with insulator surfaces even at low temperatures and energies above 60 eV.[33,35] At the same time, surface defect generation of the substrate due to electron irradiation is sufficiently reduced to allow LEED $I(V)$ experiments without indications of surface damage for hours.

LEED diffraction patterns were recorded by means of a 12 bit slow-scan charge-coupled device (CCD) camera (OES). All images were corrected for external stray light and the dark current of the CCD chip. The integration of diffraction peaks was performed by an integration procedure similar to that described in Ref. 36

The LEED experiment was performed under normal incidence conditions. The latter was checked by the coincidence of maxima and minima of the integrated intensities of symmetry equivalent diffraction peaks. LEED diffraction patterns were recorded in the energy range of 70 up to 320 eV in steps of 2 eV at 230, 160, 100, and 25 K. At each temperature, the channel-plate voltage of the MCPLEED optics and thus the relative amplification factor were adjusted in order to cover the full dynamic range of the image acquisition system. Sets of experimental $I(V)$ curves for the beam orders (10), (11), (20), and (21) are shown in diagram (A) of Fig. 1. Fine structure in the various LEED spectra shown in Fig. 1 is reproducible in experiments with different NaCl(100) cleavage planes of high quality. In particular, the set of $I(V)$ curves collected at 25 K can be directly compared to spectra published in Ref. 35.

III. TENSOR LEED ANALYSIS

The LEED $I(V)$ analysis of the data presented in Fig. 1(a) was performed using the ERLANGEN tensor LEED package developed by Blum and Heinz.[30] With this program, it is possible to optimize a large number of structural parameters by calculation and subsequent comparison of calculated $I(V)$ curves with the experimental data. The search for the best-fit structure is equivalent to the minimization of a reliability factor, which measures the agreement between calculated and experimental intensities. In the present work, the reliability factor proposed by Pendry has been used.[38]

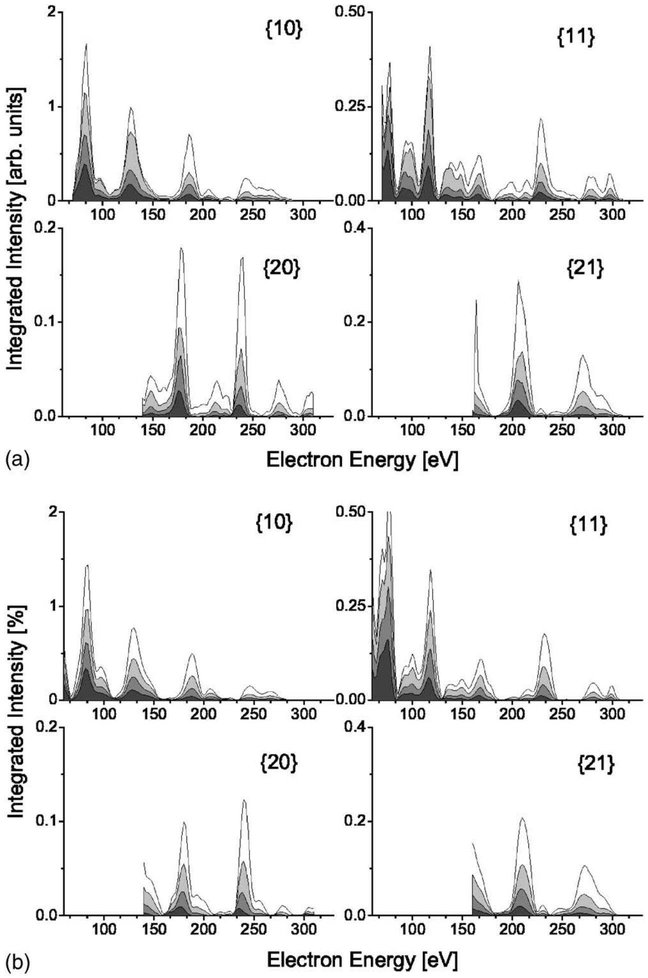

FIG. 1. (a) Measured integrated diffraction peak intensities as a function of electron energy from the bare NaCl(100) surface at 25 K (white), 100 K (light gray), 160 K (gray), and 230 K (dark gray). The intensities of the $I(E)$ curves of the various peaks are scaled in the same arbitrary units. (b) Absolute backscattered intensities of diffraction peaks as a function electron energy obtained from the tensor LEED analysis (best fit).

The structure model of the NaCl(100) surface was similar to that described in Ref. 35 and involved vertical displacements of the Na^+ and Cl^- ions in the first and the second layers (see Fig. 2). These displacements are measured with respect to a reference structure, which was NaCl bulk structure, truncated ideally in the (100) plane. Displacements are denoted in the following as $\Delta x_{i,l}$, where i represents the chemical element and l the layer. Lateral static displacements of the ions at the surface with respect to the respective bulk positions are excluded due to the C_{4v} point symmetry deduced from the observed (1×1) LEED patterns and the assumption that domains with lateral static displacements are energetically unfavored. In addition, isotropic rms vibrational amplitudes $\bar{u}_{i,l}$ of the various atoms were optimized as

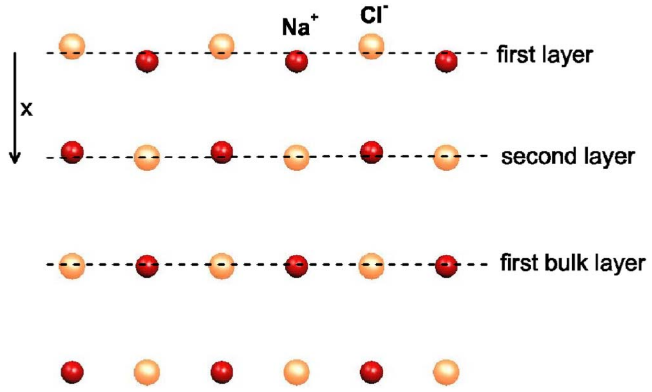

FIG. 2. (Color online) Structure model of the NaCl(100) surface (side view). A possible relaxation of the NaCl(100) surface can involve only vertical static displacements of ions, which are considered for the topmost two layers. Vibrational amplitudes and positions of ions in the third and in deeper layers are fixed to the respective bulk values.

nonstructural parameters. These are defined by means of $\bar{u}_{i,l}=\sqrt{\langle \bar{u}_{i,l}^2\rangle}$, where

$$\langle \bar{u}^2\rangle = \langle u_x^2\rangle + \langle u_y^2\rangle + \langle u_z^2\rangle \qquad (1)$$

is the isotropic mean-square amplitude. Positions and rms amplitudes of the ions in the third layer and in deeper layers were set to the respective bulk values and were not changed during the structure search. The bulk values of $\bar{u}_{\text{Na}}$ and $\bar{u}_{\text{Cl}}$ were taken from shell-model calculations of bulk NaCl,[39] which are for $T=300$ K in good agreement with experimental results from x-ray diffraction.[40] The lattice parameters of bulk NaCl at different temperatures, as well as the bulk values for the rms amplitudes of the ions, were taken from Ref. 41 and are tabulated in Table I.

The structural analysis was performed for each crystal temperature separately in several steps, the first step being a fully dynamic calculation of the wave amplitudes of an electron which is scattered at the reference structure. For the calculation of the electron wave amplitudes with the layer doubling method,[30] phase shifts with angular momentum up to $L=7$ were taken into account. These phase shifts as well as the imaginary part of the inner potential $V_i=3$ eV were taken from Ref. 35. This low value for V_i is consistent with the comparatively narrow peak shapes in the LEED spectra of Fig. 1. V_i was not varied during the structural analysis.

Chemical disorder due to anion vacancies (color centers),[37] which could influence diffraction peak intensities from a defective surface, was not included in the structure model. This is justified by the high quality of the NaCl(100) cleavage plane used in the experiment and the conditions of low electron irradiation.

The second step of the structural analysis was the calculation of amplitude changes of the scattered electron upon distortion of the reference structure. Such distortion involved displacements of ions from their reference positions or changes of their vibrational amplitude. Subsequent to these calculations followed the actual search for the best-fit structure using the search algorithm proposed by Kottcke and Heinz.[42] The search was based on a set of 200 trial structures, which were optimized independently within 10 000 search steps.

TABLE I. Static displacements Δx and average rms vibrational amplitudes $\bar{u}$ of ions in the first and the second layers of the NaCl(100) surface obtained from tensor LEED structural analysis. Values in parentheses denote error bars in units of the last decimal place of the corresponding absolute value. The optimum Pendry R factors R_P of the best-fit geometries are also given. The structure searches were based on the tabulated bulk lattice constants a and bulk rms amplitudes $\bar{u}_{i,bulk}$ taken from Refs. 41 and 39.

Temperature (K)	25	100	160	230
	First layer			
$\Delta x_{\text{Na},1}$ (Å)	+0.076(34)	+0.088(18)	+0.092(19)	+0.088(26)
$\Delta x_{\text{Cl},1}$ (Å)	−0.014(11)	−0.008(11)	−0.000(9)	+0.028(10)
$\bar{u}_{\text{Na},1}$ (Å)	0.19(5)	0.20(4)	0.24(3)	0.27(4)
$\bar{u}_{\text{Cl},1}$ (Å)	0.17(2)	0.20(2)	0.23(2)	0.26(3)
	Second layer			
$\Delta x_{\text{Na},2}$ (Å)	−0.026(21)	−0.018(17)	−0.032(10)	−0.018(17)
$\Delta x_{\text{Cl},2}$ (Å)	+0.024(11)	+0.024(8)	+0.022(5)	+0.034(10)
$\bar{u}_{\text{Na},2}$ (Å)	0.15(4)	0.18(4)	0.20(3)	0.24(4)
$\bar{u}_{\text{Cl},2}$ (Å)	0.11(3)	0.15(2)	0.17(2)	0.20(3)
V_0 (eV)	−13.8	−12.2	−12.1	−13.8
R_P	0.126	0.127	0.121	0.170
a (Å)	5.595	5.600	5.609	5.629
$\bar{u}_{\text{Na},bulk}$ (Å)	0.13	0.15	0.18	0.22
$\bar{u}_{\text{Cl},bulk}$ (Å)	0.11	0.14	0.17	0.20

The results of the structural analysis are tabulated in Table I, together with the overall Pendry R factor and the obtained real part of the inner potential. The error bars of the structure search are indicated in parentheses in units of the last decimal place of the obtained absolute value, respectively. The error bars have been estimated by means of Pendry's definition.[38] The resulting best-fit $I(V)$ curves at the considered temperatures are shown in diagram (b) of Fig. 1 in units of absolute backscattered intensity. As also reflected by the R_P values, the overall agreement between measured $I(V)$ data in diagram (a) and calculated absolute intensities in diagram (b) is very good. The largest differences are recognized in the profiles of the (20) beam. It is worth to mention that also the agreement between measured and calculated absolute intensities is good, although the Pendry R factor essentially minimizes differences of the logarithmic derivatives in the $I(V)$ curves and not differences of absolute intensities.[28,38] The $I(V)$ analysis of the data set recorded at the highest temperature results in a higher R_P of 0.17. The worse agreement is due to the uncertainties in integrating diffraction peaks with very low brightness at higher temperatures. As a consequence, some of the fine structure was below the detection limit.

TABLE II. Average layer distances *d* and rumpling parameter δ of the first two layers of the NaCl(100) surface, derived from the static displacements of ions (see Table I). All values are given in Å. The results are compared to previously reported TLEED studies and theoretical results from shell-model (SM), rigid-ion (RI), and cluster Hartree-Fock (HF) calculations.

	d_1	δ_1	d_2	δ_2
TLEED (this work)				
25 K	2.77(4)	+0.05(2)	2.80(2)	−0.03(2)
100 K	2.76(3)	+0.05(2)	2.80(1)	−0.02(1)
160 K	2.76(2)	+0.05(2)	2.80(1)	−0.03(1)
230 K	2.77(3)	+0.03(2)	2.81(1)	−0.03(2)
TLEED, Ref. 35 (20 K)	2.76(2)	+0.07(3)	2.80(3)	−0.01(4)
TLEED, Ref. 43 (110 K)	2.79	+0.06	2.79	+0.01
SM, Ref. 19 (a=5.59 Å)	2.72	+0.09	2.84	−0.05
SM, Ref. 20 (a=5.60 Å)	2.78	+0.04	2.80	−0.02
RI, Ref. 15		+0.04		
HF, Ref. 14 (a=5.58 Å)	2.76	+0.01		

IV. DISCUSSION

According to the results of the present LEED study (see Table I), the NaCl(100) surface exhibits a slight rumpling, which is characterized by a static inward shift of the Na^+ ion in the topmost layer of 0.08–0.09 Å with an error of 0.03 Å. The static displacements of the other ions in the first two layers are small. Due to the smaller error bars in the positions of the anions, however, a slight shift of Cl^- ions in the second layer toward the bulk seems significant. A significant influence of temperature on the relative equilibrium positions of the ions, apart from the considered general lattice expansion, cannot be deduced and was also not expected in the investigated temperature range. This is also seen in Table II, where the resulting average layer distances d_i and the average rumpling δ_i are tabulated together with the results of recent experimental and theoretical studies. Following the definition used in Ref. 35, the rumpling parameter may be defined as

$$\delta_i = \frac{1}{2}(\Delta x_{\mathrm{Na},i} - \Delta x_{\mathrm{Cl},i}). \tag{2}$$

As can be seen in Table II, the present results are in reasonable agreement with previous automated tensor LEED studies.[35,43] The rumpling δ_1 of the topmost layer is, however, slightly smaller. The relaxation of the NaCl(100) surface has been investigated in the past in various theoretical studies. Shell-model (SM) calculations by Benson *et al.*[19] seem to overestimate the surface relaxation of the NaCl(100) surface, while the SM results of de Wette *et al.* are in good agreement with the experimentally determined relaxation.

Molecular mechanics calculations using a rigid-ion (RI) potential[15] lead to the same surface rumpling, although polarization forces of ions are completely neglected.[15] Finally, embedded cluster Hartree-Fock (HF) calculations reported by Puchin *et al.*[14] are in excellent agreement with the present work concerning the contraction of the layer distance d_1. However, since the HF study reports inward displacements of both the Na^+ and the Cl^- in the first layer, the surface rumpling is very small.

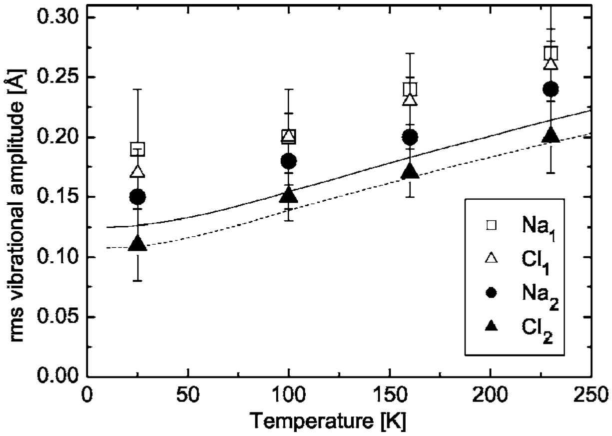

FIG. 3. rms vibrational amplitudes at the NaCl(100) single crystal surface as a function of temperature. The solid and the dashed lines represent the temperature dependent rms vibrational amplitudes of bulk sodium and chlorine, respectively, according to Gupta (Ref. 39).

The main interest of the present study focuses on the rms vibrational amplitudes of the surface ions. These are given in Table I and are also plotted in Fig. 3. Despite the large error bars, the following trends are observed: The expected increase of vibrational amplitudes of all types of ions with increasing temperature is clearly observed. The vibrational amplitudes of the ions in the first layer are larger than those of the second layer at all investigated temperatures. At the same time, the rms amplitudes of the ions in the second layer are already close to the respective bulk values. A slight enhancement of $\bar{u}_{\mathrm{Na},2}$ is not significant, but it is recognized that the amplitudes of the sodium ions in the second layer are larger than those of the anions. Contrary to this, the rms amplitudes of chlorine in the topmost layer appear nearly as large as those of the topmost sodium ions. Chen *et al.*[23] report lattice dynamics calculations using RI potentials, which predict equal vibrational amplitudes of the ions in the topmost layer at room temperature. As discussed in Ref. 23, this is explained by the invariance of force constants under an interchange of anions and cations in the RI model. Moreover, these authors report mean-square displacements of surface ions as a function of temperature, from which isotropic rms vibrational amplitudes can be derived. For 100, 160, and 230 K, these are in excellent agreement with the values for $\bar{u}$ in Table I.

In order to compare the present results with room-temperature MSAs, which were calculated by Chen and Aldredge using a shell model,[24] isotropic MSAs were calculated from the experimental data in Fig. 3 and extrapolated to T=300 K. As can be seen in Table III, these extrapolated MSAs for ions in the first layer are slightly higher than those predicted by theory; however, within the statistical error, they agree with the isotropic MSAs derived from the SM calculations and, moreover, also with those from the deformation-dipole (DD) model according to Schulze.[22,24]

TABLE III. Extrapolated experimental room-temperature (300 K) isotropic mean-square amplitudes of the Na^+ and Cl^- ions in the first two layers of the NaCl(100) surface in comparison with MSAs derived from shell model (SM) and deformation-dipole (DD) model. Values in parentheses denote statistical errors of the extrapolation in units of the last decimal place of the absolute value. All values are given in units of $Å^2$.

	$\langle\bar{u}^2\rangle_{Na,1}$	$\langle\bar{u}^2\rangle_{Cl,1}$	$\langle\bar{u}^2\rangle_{Na,2}$	$\langle\bar{u}^2\rangle_{Cl,2}$
TLEED (this work)	0.09(1)	0.08(1)	0.07(2)	0.05(1)
			Bulk values	
	$\langle\bar{u}^2\rangle_{Na,1}$	$\langle\bar{u}^2\rangle_{Cl,1}$	$\langle\bar{u}^2\rangle_{Na,2}$	$\langle\bar{u}^2\rangle_{Cl,2}$
SM (Ref. 24)	0.080	0.069	0.060	0.051
DD (Refs. 22 and 24)	0.081	0.076	0.063	0.057
SM (Ref. 39)			0.059	0.049

Furthermore, the extrapolated MSAs of the ions in the second layer are in good agreement with the calculated isotropic bulk MSAs.

In the low-temperature limit, however, the RI model by Chen and Alldredge predicts MSAs which are consistent with surface rms amplitudes $\bar{u}_{Na,1}=0.14$ Å and $\bar{u}_{Cl,1}=0.13$ Å. The latter are smaller than the corresponding experimental data. A similar behavior is also seen, if the present results are compared to MSAs reported by Schulze.[22] A trivial experimental reason for the higher low-temperature vibrational amplitudes of the ions in the first layer could, at first sight, be an inaccurate temperature measurement, but this is immediately excluded, on the one hand, by an inspection of experimental beam intensities in Fig. 1 and, on the other hand, by the measured rms amplitude of chlorine in the second layer, which is, as can be seen in Fig. 3, in excellent agreement with the theoretical prediction for bulk Cl^-. Another reason for the higher amplitudes of the ions in the topmost layer could be an effect of static disorder in real NaCl(100) surfaces. Static disorder can never be excluded[10] and should contribute in a similar way as the lattice distortion due to the zero-temperature vibrations of ions. On the other hand, it should be pointed out that the various lattice-dynamical models neglect the effects of anharmonicity and assume, moreover, an unrelaxed interface.[24] Anharmonic effects, however, should become more important at higher temperatures. In view of the good agreement of experiment and theory at room temperature (see Table III), the neglect of anharmonic effects is unlikely to be responsible for the discrepancies between experiment and theory at low temperatures.

Another point for discussion is the use of isotropic vibrational amplitudes of ions in the LEED analysis. The assumption of isotropic rms vibrational amplitudes seems reasonable for ions in the bulk layers,[24] although a study of the Debye-Waller factors of bulk NaCl using the Mössbauer effect gave indications for a nonisotropic thermal cloud of ions in this cubic material.[44] The good agreement between measured vibrational amplitudes in the second layer with calculated isotropic bulk amplitudes supports the assumption that the ion dynamics in the second layer is isotropic. According to the SM calculations by Chen and Alldredge, the enhancement factors of MSAs of surface ions are, however, anisotropic. At room temperature, for example, the Na^+ ion in the topmost layer is expected to have $\langle u_\perp^2\rangle=0.032$ $Å^2$ in the direction perpendicular to the surface but only $\langle u_\parallel^2\rangle=0.024$ $Å^2$ parallel to the surface.[24] The fact that the experimentally determined isotropic surface vibrational amplitudes reported in this study are, in general, higher than predicted by theory could thus be explained by the higher sensitivity of the LEED experiments for structural and dynamical properties perpendicular to the surface,[28] which, in the case of NaCl(100), would lead to a systematic overestimation of the vibrational amplitudes parallel to the surface.

The extension of the TLEED analysis to anisotropic vibrational amplitudes requires a higher computational effort but is, in principle, possible[45] and shall be envisaged also for other alkali halides in the near future. The present results, however, already show that in the case of the NaCl(100) surface, an extraordinarily good agreement between experiment and theory regarding its structural and dynamical properties can be recognized. Experiment and various theoretical models agree that the enhancement factors of the mean-square amplitudes of the ions at the interface are smaller than a factor of 2. Lattice dynamics in the quasiharmonic approximation is, as it seems, appropriate to give a detailed description of the dynamics of the NaCl(100) surface in the temperature range below 300 K.

V. SUMMARY

The surface relaxation and vibrational amplitudes of the ions at the NaCl(100) surface were investigated experimentally by means of low-energy electron diffraction. Diffraction peak intensities of four inequivalent beam orders were determined at 25, 100, 160, and 230 K as a function of electron energy. The resulting $I(V)$ curves were analyzed using the tensor LEED approach in the approximation of isotropic vibrational amplitudes of surface ions.

According to the $I(V)$ analysis, the NaCl(100) surface exhibits a significant relaxation, characterized by a static displacement of the Na^+ ions toward the bulk of 0.08–0.09 Å, in reasonable agreement with previous studies.[35,43] Except for the general lattice expansion considered in the structure models, no significant change of surface structure was discernible in the investigated temperature range.

As expected, a significant effect of temperature on the root-mean-square (rms) amplitudes could be deduced. According to the LEED experiment, the rms amplitudes of the Na^+ and Cl^- ions in the topmost layer are enhanced compared to the respective bulk values. At 230 K, these amplitudes are 0.27 ± 0.04 Å for Na^+ and 0.26 ± 0.03 Å for Cl^- and are thus equal within the error bars. In agreement with recent theoretical studies, the enhancement factors of the surface and bulk mean-square amplitudes (MSAs) of the ions are smaller than 2 at temperatures above 100 K. At 25 K, the LEED experiment favors higher vibrational amplitudes than predicted by model calculations.[22–24] This was attributed to systematic errors due to a possible amount of static disorder at the real NaCl(100) surface and, moreover, to the higher sensitivity of the LEED experiment for the larger out-of-plane displacements of ions, which, in an isotropic model of thermal disorder, leads to an overestimation of the in-plane vibrational amplitudes in the surface layer. Good agreement of the vibrational amplitudes of ions in the second layer with those of the respective bulk ions was found in the whole investigated temperature range.

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*Electronic address: jochen.vogt@vst.uni-magdeburg.de

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