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The structure and lattice dynamics of RbBr(100) and RbI(100) single crystal surfaces: A tensor low energy electron diffraction analysis

S. Härtel, J. Vogt, H. Weiss *

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

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ABSTRACT

The structure and lattice dynamics of RbBr(100) and RbI(100) single crystal surfaces cleaved under UHV conditions were investigated by means of low energy electron diffraction (LEED) at temperatures of 156 K and 183 K, respectively. Since RbBr and RbI are insulators the experiments were carried out with a microchannel plate LEED system at very low primary currents (~5 nA). For both materials four different diffraction orders could be observed. Diffraction patterns were recorded over an energy range from 30 eV to 220 eV in increments of 2 eV and *I*(*V*) curves for each spot were extracted. The *I*(*V*) curves were analyzed using the tensor LEED approach. For both alkali halide substrates surface structures of (1×1) periodicity close to the truncated bulk structure were found. For RbBr, the first interlayer distance is reduced by about 2.2%, where the Rb^+ cations in the topmost layer are shifted inwards by 0.06(3) Å, and the anions also exhibit an inward shift which is however smaller (0.04(3) Å). The root mean square vibrational amplitudes are enlarged by a factor of 1.3 for Rb^+ and 1.25 for Br^-, respectively. For RbI(100) the cations of the topmost layer are shifted inwards by 0.07(3) Å and the anions outwards by 0.02(1) Å. The vibrational amplitudes of the ions are not enlarged as for RbBr but close to the corresponding bulk values.

1. Introduction

Bare and adsorbate-covered alkali halide surfaces have been the topic of numerous experimental and theoretical investigations over the last decades, and continue to be interesting research objects due to their seeming simplicity. For such studies, knowledge of the arrangement of the ions in the topmost layers and their vibrational amplitudes is important for the understanding of surface-related phenomena, like surface phonon dynamics and adsorption. However one of the most prominent standard techniques for the determination of these parameters, low energy electron diffraction (LEED), can cause surface charging and surface damage when a conventional LEED system with primary electron currents in the range of μA is used. This problem can be avoided by the use of a microchannel plate LEED system which was also applied in the present work. The microchannel plates amplify the diffracted electrons by at least 4 orders of magnitude which allows to use primary electron currents in the range of nA. With this technique we have shown that it is possible to determine structural parameters of different bare and adsorbate-covered alkali halide single crystal surfaces with high precision [1–4]. In addition, the determination of the mean square amplitudes (MSAs) of the topmost ions is possible [5,6].

With LEED at very low currents as well as some other techniques the surface relaxation and rumpling of several bare alkali halides have been investigated experimentally during the last decade [1,2,7–11]. The theoretical approaches for the surface relaxation of insulator surfaces mainly base on shell models (e.g. [12,13]) but recently also DFT calculations were published [14]. In general, the models predict inward shifts of the cations and (smaller) outward shifts of the anions for the topmost layer, corresponding to a layer rumpling and a contraction of the interlayer distance. The available experimental results for the different compounds are in more or less good agreement to theory. For the NaCl(100) surface Vogt and Weiss [1] as well as Roberts et al. [7] measured by means of LEED a small but significant contraction of the first interlayer distance by about 1.4% and a rumpling of about 2.5% (compared to the bulk spacing) which matches quite well the theoretical results published by Benson and Claxton [12] and de Wette et al. [13]. It is interesting to note that in one case the NaCl(100) was epitaxially grown on Pt(111) and Pd(100) surfaces [7], while it was a cleaved NaCl single crystal in the other [1]. However the available experimental values for LiF(100) differ considerably. While Roberts et al. [8] measured a vertical displacement of the first layer ions as well as a contraction of the first interlayer distance of 12% each compared to the bulk, Vogt and Weiss determined a practically unchanged value for the first interlayer distance of 2.01 Å [2] although both surfaces were investigated by LEED. The latter result is in good agreement with

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* Corresponding author. Tel.: +49 391 67 18416; fax: +49 391 67 11387.
E-mail address: helmut.weiss@ovgu.de (H. Weiss).

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theoretical predictions [13]. We attribute the discrepancy between the experimental results to the fact that in the experiments by Roberts et al. thin LiF(100) films grown on Pt(111) were used.

This result suggests that a structural determination of bare insulator surfaces may give more reliable results when performed on single crystals. In the present study we extend our previous investigations on the (100) planes of NaCl, KBr, KCl and LiF to RbBr and RbI. The goal is not only to test the agreement between experiment and theory for additional systems, but also to obtain a reliable data base for future adsorption experiments. Weakly bound physisorbates on alkali halides behave to some extent like two-dimensional molecular crystals (see e.g. [3,4]), with a delicate balance between lateral forces within the layer, and forces between individual adsorbed atoms or molecules and the surface.

As far as we know there are hardly any other experimental results yet for rubidium halide single crystal surfaces. By means of inelastic He-atom scattering Chern et al. estimated a corrugation of 0.4 Å for the RbBr(100) surface [15]. Okazawa et al. examined the RbI(100) surface by using MEIS (medium energy ion scattering). They obtained a rumpling of 0.05 Å for the topmost layer and a contraction of 1.7% for the first interlayer distance [9], in reasonable agreement with the calculations of Benson and Claxton [12]. Furthermore they studied the anisotropic vibrational amplitudes of RbI(100) by MEIS and molecular dynamics simulations and determined values for the topmost layer which are enhanced compared to the bulk by factors of about 1.22 for Rb^+ and 1.27 for I^-, respectively [16].

The paper is organized as follows. A brief description of the experimental setup is given in Section 2. In Section 3 the experimental results for RbBr and RbI, a brief sketch of the tensor LEED analysis and a detailed description of the resulting ion positions and vibrational amplitudes are presented. A summary and an outlook follow in Section 4.

2. Experimental

The main components of the experimental setup are an UHV chamber, a commercial microchannel plate LEED system (MCP-LEED, OMICRON), and a cryostat. The cleavage planes of the single crystals had to be prepared under UHV conditions because of the strong hygroscopicity of RbBr and RbI. Therefore the UHV chamber is equipped with a cleavage gripper which allows to cleave the crystals *in situ*. The RbBr and RbI single crystals (Korth, 10 × 10 mm, with initial thickness of about 10 mm before cleavage) were mounted on an OFHC (oxygen free high conductivity) copper sample holder which is thermally coupled to the cryostat. The coolant was liquid nitrogen. With this setup crystal temperatures down to 146 K were reached and the pressure during the experiments was $\sim 1 \times 10^{-10}$ mbar. For exact sample positioning, the sample holder can be rotated by 360°, tilted, and shifted in x,y,z-direction. The two channel plates of the LEED system amplify the diffracted electrons which makes it possible to carry out the experiments with primary currents in the range of only ~5 nA. Diffraction patterns were measured under normal incidence between 30 and 220 eV. The normal incidence condition of the primary electron beam is controlled by ensuring symmetry of all beams of equal diffraction order.

The diffraction patterns were recorded with a slow-speed integrating CCD camera which is equipped with an optical filter in order to match the emission of the phosphorous screen of the LEED instrument and to suppress background radiation. The energy step width was 2 eV and the integration time on the CCD chip of the camera 2 s. Each diffraction pattern was background-corrected by recording an image with blocked electron beam immediately after the latter in order to subtract stray light from the filaments in the UHV chamber. The crystal surfaces were exposed to the electrons only during the time of data acquisition. Within the measured energy range there was no evidence for charging effects as well as for surface damage. A simple calculation shows that under these conditions the sample surface is exposed to only $\sim 0.64\ \mu C\,cm^{-2}$, i.e. only about each second unit cell is hit by an electron.

The $I(V)$ curves were generated from these patterns by extracting background-corrected beam intensities with an integration method similar to that given by Held et al. [17], and used in our previous studies [1–5].

3. Results and discussion

3.1. Diffraction patterns and I(V) curves

A LEED pattern of a clean RbBr(100) surface for a primary electron energy of 86 eV at a temperature of $T = 156$ K is shown in Fig. 1 (on the left). For the $I(V)$ analysis LEED patterns were recorded in an energy range from 30 eV to 220 eV with increments of 2 eV. The extracted $I(V)$ curves for the (10), (11), (20), and (21) spots are shown in Fig. 2 as solid lines together with the best-fit theoretical curves (dashed lines). Diffraction spots of higher order could not be observed due to the limited viewing angle of only 70° for the MCP-LEED. For RbI(100) $I(V)$ data were measured from 36 eV to 220 eV at a temperature of $T = 183$K. A LEED pattern at 68 eV is also shown in Fig. 1 (on the right). For RbI also four different diffraction orders could be observed. The RbI(100) $I(V)$ curves extracted from the LEED patterns are shown in Fig. 3 (together with the best-fit theoretical curves).

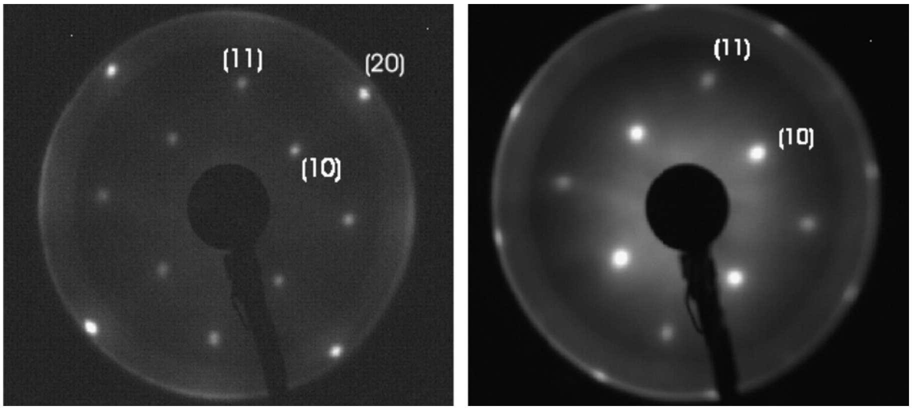

Fig. 1. Left: LEED pattern of the RbBr(100) surface at a primary electron energy of 86 eV and a temperature of 156 K. Right: LEED pattern of the RbI(100) surface at 68 eV and 183 K.