# Scanning Tunneling Spectroscopy of Cl Vacancies in NaCl Films: Strong Electron-Phonon Coupling in Double-Barrier Tunneling Junctions

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Broad Gaussian line shapes are observed in scanning tunneling spectroscopy of single, localized electronic states induced by Cl vacancies in ultrathin NaCl films on Cu surfaces. Using a simple inelastic resonance tunneling model, we show that the observed broad line shapes are caused by a strong coupling between the localized state and the optical phonons in the film. The parameters for the model are obtained from density functional calculations, in which the occupation of the vacancy state temporarily taking place in the experiment has also been accounted for.

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The recent spectacular progress in carrying out scanning tunneling microscopy (STM) and spectroscopy (STS) of adsorbates on ultrathin, insulating films supported by metal surfaces has opened up a new fascinating field in atomic-scale science [1–4]. This field is of key importance, for example, in the realization of any future atomic-scale electronics that will necessarily be based on nanostructures hosting confined electronic states, which are insulated from the environment by nanostructured, wide-band-gap materials. A fundamental issue is the degree of decoupling of localized electronic states by an insulating film. The well-known lifetime broadening—the dominant broadening mechanism for localized electronic states on metal surfaces—should be dramatically reduced by an insulating film. Therefore, it could be expected that the adsorbate and defect-induced states on insulators exhibit very small linewidths. However, recent STS experiments revealed the contrary [5,6]. This apparent contradiction triggered this study on the different broadening mechanisms and resulting line shapes and widths in STS.

An ideal model system for the study of tunneling through a localized electronic state decoupled by a polar insulator from the metal substrate and the associated line shape is provided by a single Cl vacancy in NaCl films on Cu surfaces. This atomic-scale defect in an otherwise defect-free environment is fairly simple, well defined, and stable. The intrinsic defects in bulk and at surfaces of NaCl have been studied both experimentally and theoretically in detail [7–9]. These studies have shown that a Cl vacancy, which is commonly referred to as a color or $F$ center, introduces a singly occupied defect state in the bulk band gap.

In this Letter, we show from STM and STS measurements that a single Cl vacancy in a NaCl film on a Cu surface introduces an unoccupied vacancy state (VS) with a broad Gaussian line shape in the $dI/dV$ spectra. Using a simple inelastic resonance tunneling model with parameters from density functional calculations, we show that the observed line shape is caused by a strong electron-phonon ($e$-ph) coupling of the VS to the ionic lattice of the insulating film. This broadening mechanism should be a general phenomenon for defect and adsorbate states on polar, insulating films. For example, it provides an explanation of the recently observed, Gaussian broadening of the negative ion resonance in pentacene molecules adsorbed on NaCl films [5]. In addition, the positive charge of the vacancy is confirmed on the Cu(111) surface by the formation of interface-state localization (ISL) at the vacancy.

The experiments were carried out with a home-built low-temperature STM operated at $T = 5$ K. Cu(111), Cu(100), and Cu(311) single-crystal samples were cleaned by several sputtering and annealing cycles. NaCl was evaporated thermally, keeping the sample temperature at about 300 K, so that defect-free, (100)-terminated NaCl islands with few atomic layers were formed [1,10–12]. Bias voltages refer to the sample voltage with respect to the tip. Cl vacancies were formed with the STM tip using two different techniques [13].

To obtain a better physical insight into the nature of these vacancies, we have carried out density-functional theory (DFT) calculations of their geometry and electronic states. The calculations were based on a plane wave basis set and a projector augmented wave method [14,15], as implemented in the VASP code [16] [for details, see Ref. [17]]. Because growth of the NaCl films on Cu(111) is incommensurate, the calculations were limited to films supported by Cu(100) and Cu(311) surfaces. STM images were simulated using the Tersoff-Hamann approximation [18] in which STM images correspond to topographic images of constant local density of sample states (LDOS) at the Fermi energy and at the position of the tip apex. Finally, parameters for the $e$-ph coupling model were calculated using a $\Delta$SCF-like scheme [19] within DFT as described below.

In STM, $Cl^-$ ions are imaged as protrusions on NaCl films [20–22]. As illustrated in Fig. 1(a) for the NaCl

 

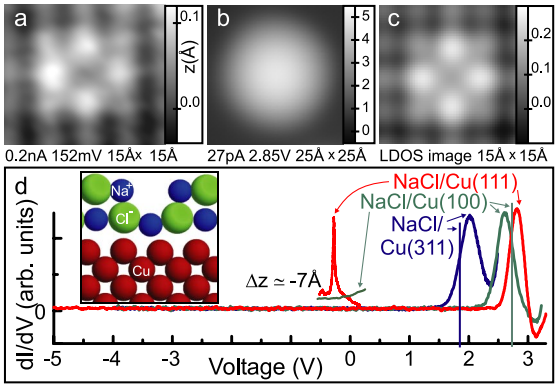


FIG. 1 (color online). Experimental (a), (b) and simulated STM images (c) of an individual Cl vacancy in the top layer of a bilayer of NaCl on Cu(111) (a), (b) and Cu(100) (c). Whereas the low-bias image (a), (c) shows a missing protrusion, the image at high bias voltage (b) shows a large protrusion of 4.5 Å in height. (d) $dI/dV$ spectra at a Cl vacancy in a bilayer of NaCl on Cu(311), Cu(100), and Cu(111). The calculated peak positions are shown as vertical lines for NaCl bilayer on Cu(311) and Cu(100). In the case of NaCl/Cu(111), there is an additional peak at $-0.26$ V that can be resolved only when taking a spectrum with the tip being about $\Delta z \simeq -7$ Å closer to the surface. In the inset a sphere model of the vacancy geometry is shown.

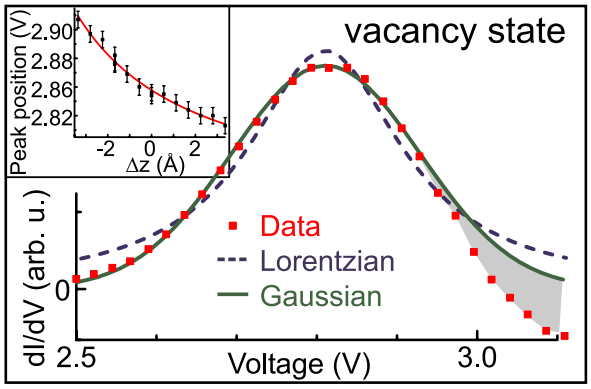


FIG. 2 (color online). $dI/dV$ spectrum of the VS in a bilayer of NaCl on Cu(111) fitted to Lorentzian and Gaussian line shapes. The slight deviation from the Gaussian (shaded area) is in agreement with the tunneling barrier being modified by the applied voltage [33]. Inset: VS peak position for varying tip-surface distances. The best fit to a 1D capacitor model [4] is indicated by a solid line. $\Delta z = 0$ refers to a current of 1.5 pA.

bilayer on Cu(111), the Cl vacancies are imaged as missing protrusions accompanied by an increase in the corrugation of the adjacent Cl ions [23]. The assignment of the created defects to single Cl vacancies is verified by comparing the simulated and observed STM images in Fig. 1. The enhanced corrugation of the adjacent protrusions is caused by the outward relaxation of the $Cl^-$ ions. As shown by the $dI/dV$ spectra in Fig. 1(d), the Cl vacancy in a NaCl bilayer on Cu(311), Cu(100), and Cu(111) induces an unoccupied VS at 2.03, 2.57, and 2.83 V, respectively. The peak positions follow roughly the differences in work functions for the clean Cu facets. The state is localized at the vacancy site, and for voltages exceeding the VS energy the tunneling is dramatically enhanced by 4 orders of magnitude compared to tunneling through the defect-free bilayer. This is revealed by the large protrusion of about 4.5 Å in height in the STM image [Fig. 1(b)].

In the case of a double-barrier tunneling junction, one needs to correct for the voltage drop across the insulating film to obtain the energy of the VS in the absence of an applied electric field. The electric field and thus the voltage drop depend on the tip-surface distance $z + \Delta z$. As shown in the inset of Fig. 2 for the NaCl bilayer on Cu(111), we find that the peak position shifts only slightly with $\Delta z$. Using a simple one-dimensional (1D) capacitor model [4], we estimate the VS energy in the absence of an external field to be $E_{VS} = 2.77 \pm 0.02$ eV. Thus, the field induced shift is only a few percent of the bias voltage applied.

We experimentally determined the charge state of the vacancy as described in the following. As shown by the STM image in the inset of Fig. 3, the Cl vacancy efficiently scatters the Shockley-like interface-state electrons [11] localized in the interface of the NaCl bilayer and Cu(111). In addition, the defect-induced potential supports an ISL [24] showing up as a peak at $-0.26$ V in the $dI/dV$ spectrum [Figs. 1(d) and 3]. This state is split off from the interface-state band just below the band bottom at $-0.22$ V [11]. This assignment is supported by the absence of such a peak in the $dI/dV$ spectra for a Cl vacancy in the NaCl bilayers on Cu(311) and Cu(100), for which no interface-state band is present near the Fermi energy. In general, an ISL is expected to exist on insulating films on Cu(111) whenever the interaction of a two-dimensional,

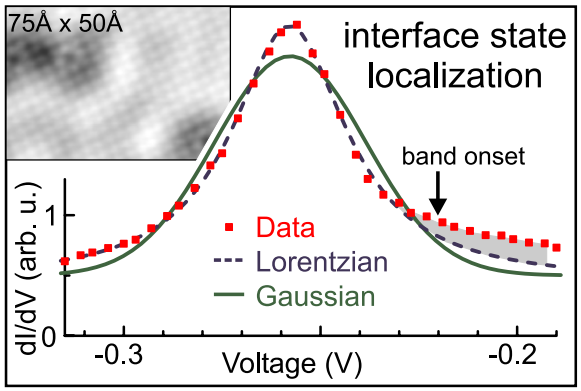


FIG. 3 (color online). $dI/dV$ spectrum of the ISL in a bilayer of NaCl on Cu(111) fitted to Lorentzian and Gaussian line shapes. The slight deviation from the Lorentzian (shaded area) is due to the remnants of the interface-state band. For comparison, the position of the onset of the interface-state band for the defect-free surface is indicated by an arrow. Inset: STM image acquired at $V = 58$ mV showing the scattering of the interface state at the vacancies.

free-electron-like interface band with a defect is attractive [24]. In the case of the Cl vacancy such an attractive interaction is consistent with the vacancy being positively charged. For a comparison, a negatively charged defect, such as an $Au^-$ ion [1], is a strong scatterer of interface-state electrons, but does not induce any ISL, whereas a neutral defect, such as an Au adatom, neither scatters the interface-state electrons nor induces an ISL. Thus, observation of the interface-state scattering and ISL provides information about the charge state of the defect. The interpretation that the vacancy is positively charged is corroborated by the calculated charge density.

The two localized states supported by a Cl vacancy in a NaCl bilayer on Cu(111) have different and characteristic line shapes in the $dI/dV$ spectra. As can be clearly seen in the Figs. 2 and 3, the VS peak is best fitted by a Gaussian, whereas the ISL peak is best fitted by a Lorentzian [25]. The corresponding full width at half maximum (FWHM) is 0.27 V for the VS and only 0.035 V for the ISL in the NaCl bilayer on Cu(111). The $dI/dV$ spectrum for the VS in the NaCl trilayer on Cu(111) also exhibits a Gaussian line shape with the same width as that for the bilayer and centered at 2.70 eV for a tunneling current of 20 pA.

Interestingly, the peak of the ISL shows a much smaller width than for the VS despite the much larger spatial overlap of the ISL with the metal states. The Lorentzian line shape of the ISL corresponds to the well-known lifetime broadening which can arise from several mechanisms [26]. In the case of the VS, the Gaussian line shape and the same FWHM values for the bilayer and trilayer cannot be easily reconciled with a broadening mechanism involving a coupling to the metal states.

Instead, we show that the broad Gaussian line shape of the VS in the $dI/dV$ spectra is a result of strong $e$-ph coupling in the tunneling through the VS. The argument is based on a simple inelastic resonance tunneling model in a double-barrier junction with linear coupling to phonon modes [27,28]. In this model for a single phonon mode with energy $\hbar\omega$, the line shape is given by a Poisson distributed set of peaks separated by $\hbar\omega$ and centered at the (vertical) electron attachment energy $\Delta E$ (Fig. 4). In the limit of strong $e$-ph coupling, the envelope of the vibronic peaks becomes a Gaussian with a FWHM of $\Delta = \sqrt{8 \ln 2 S}\hbar\omega$ where the strength of the $e$-ph coupling appears through the Huang-Rhys factor $S$. This factor can be expressed in terms of the relaxation energy $E_{\mathrm{rel}}$ (Fig. 4) of the phonon mode when the VS is occupied as $S = E_{\mathrm{rel}}/\hbar\omega$. Note that the width $\Delta$ is the same as the width of the Gaussian distribution of the electron attachment energies to the VS caused by the zero-point fluctuations of the phonon mode (Fig. 4).

The above model requires values of three parameters to describe the peak position and width: a characteristic vibrational energy $\hbar\omega$, the excitation energy $\Delta E$ that is needed to attach an extra electron to the VS for a fixed ionic geometry, and the ionic relaxation energy $E_{\mathrm{rel}}$. As a value for $\hbar\omega$, we used the longitudinal optical (LO) phonon energy of bulk NaCl, $\hbar\omega = 32$ meV [29], since this mode provides the strongest coupling to an external charge.

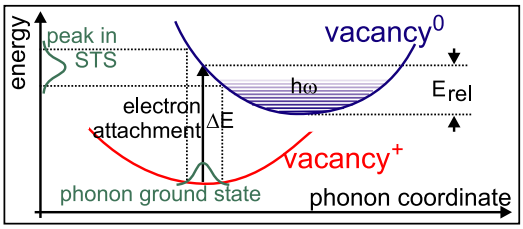


FIG. 4 (color online). Illustration of the broadening mechanism.

$\Delta E$ and $E_{\mathrm{rel}}$ were calculated using the following $\Delta$SCF-like scheme within DFT [19]. First, the calculated ground state electronic structure revealed that the VS was described by a single, unoccupied Kohn-Sham (KS) state localized at the vacancy site [30]. Note that this result supports our claim that the observed broadening of the VS is not caused by the coupling of the VS to the metal states through the film [31]. Next, this KS state was forced to be occupied by a single electron while keeping the whole system neutral by adjusting the Fermi level. $\Delta E$ was then calculated as the total energy difference between this excited state (occupied VS) in the ground state geometry and the ground state (unoccupied VS): $\Delta E = 1.85$ and 2.73 eV for the VS in the NaCl bilayer on Cu(311) and Cu(100) surfaces, respectively. Finally for Cu(100), $E_{\mathrm{rel}}$ was obtained as the gain in total energy by a full structural optimization while keeping the VS occupied: $E_{\mathrm{rel}} = 0.96$ eV.

As shown in Fig. 1(d), the calculated values for $\Delta E$ are in very good agreement with the observed VS peak positions. We find a strong $e$-ph coupling, $S = 30$, for the vacancy in a NaCl bilayer on Cu(100), being almost as strong as for a Cl vacancy state in bulk NaCl [$S = 42$ [32]]. The resulting estimate for the width, $\Delta = 0.41$ eV, accounts well for the observed FWHM of 0.32 V for the VS state of the corresponding system. Note that the discrete vibronic structure of the line shape in the model should be blurred in the spectra primarily by a vibronic contribution from a band of phonon modes.

In contrast to the VS, there is no significant broadening of the ISL due to the coupling to the optical phonons in the NaCl film. This can be understood qualitatively from the fact that the ISL wave function is similar to the Shockley interface-state wave function [11], and thus, is efficiently screened by the metal electrons.

On the other hand, any localized state that is not efficiently screened near a polar insulator is affected by the strong $e$-ph coupling as described for the VS. For example, this mechanism provides an explanation of the observation in recent STS measurements of a Gaussian-shaped peak from the negative ion resonance in pentacene on NaCl

films with a FWHM of 0.30 eV, which is way beyond the expected lifetime broadening [5]. As in the present case, the FWHM did not change from two to three layers of NaCl thickness. Strong coupling to phonons should also explain the broad peaks observed in $dI/dV$ spectra of Pd adatom states on the ultrathin polar insulating $Al_2O_3$ film on NiAl [6].

In conclusion, the observed broad line shapes in STS from defects and adsorbate-induced electronic states on ultrathin, polar films do not indicate that these films are leaky but should in general be an effect of the strong coupling of localized electronic states to optical phonons in the film. This finding comes from STM and STS studies of single Cl vacancies in and adsorbed pentacene molecules on ultrathin NaCl films on Cu surfaces. The Cl vacancies in a NaCl film exhibit an unoccupied vacancy state with a broad Gaussian line shape in the STS, which is explained in a simple inelastic resonance tunneling model with parameters from density functional calculations. Finally, useful information about the charge state of a defect or adsorbate on an insulating film on Cu(111) can be obtained from STM imaging of interface-state scattering combined with STS measurement of any induced interface-state localization.

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