Mott Insulating Ground State on a Triangular Surface Lattice

H. H. Weitering,[1,2] X. Shi,[1] P. D. Johnson,[3] J. Chen,[4] N. J. DiNardo,[5,6] and K. Kempa[7]
[1]*Department of Physics and Astronomy, The University of Tennessee, Knoxville, Tennessee 37996*
[2]*Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831*
[3]*Department of Physics, Brookhaven National Laboratory, Upton, New York 11973*
[4]*Department of Physics, University of Pennsylvania, Philadelphia, Pennsylvania 19104*
[5]*Department of Physics and Atmospheric Science, Drexel University, Philadelphia, Pennsylvania 19104*
[6]*Department of Materials Science and Engineering, University of Pennsylvania,*
Philadelphia, Pennsylvania 19104
[7]*Department of Physics, Boston College, Chestnut Hill, Massachusetts 02167*
(Received 20 September 1996)

Momentum-resolved direct and inverse photoemission spectra of the K/Si(111)-$(\sqrt{3} \times \sqrt{3})R30°$-B interface reveals the presence of strongly localized surface states. The K overlayer remains nonmetallic up to the saturation coverage. This system most likely presents the first experimental realization of a frustrated spin 1/2 Heisenberg antiferromagnet on a two-dimensional triangular lattice. [S0031-9007(97)02423-X]

PACS numbers: 73.20.At, 71.30.+h, 75.30.Pd, 79.60.Dp

The band theory of solids has been remarkably successful in describing the ground state properties of many crystalline materials. Nonetheless, limitations to this theory were already pointed out in 1937 by de Boer and Verwey who argued that NiO, which is an optically transparent insulator, would be metallic according to band theory [1]. Fascinating examples of the breakdown of band theory include the high T_c superconductors [2] and doped fullerenes [3]. In simple terms, band theory breaks down when the Coulomb repulsion U between electrons on a lattice site is comparable to or larger than the *single particle* bandwidth, W [1]. If the ratio $U/W \gtrsim 1$, the charge carriers no longer delocalize but condense at the ion cores, leading to an insulating antiferromagnetic ground state at half filling (i.e., a Mott-Hubbard insulator).

Surfaces and interfaces represent a special class of narrow band systems. Many semiconductor surfaces possess dangling-bond-derived surface states with bandwidths $\lesssim$1 eV. Estimates indicate that the effective Coulomb interactions, U_{eff}, within the dangling bonds of an ideally truncated Si(111) surface are on the order of $\approx$1 eV [4,5] which brings the Si(111) surface in the Mott-Hubbard regime. However, Si(111) does not become an antiferromagnetic insulator because it largely eliminates its dangling bonds by forming a (7×7) superstructure [6]. Likewise, it was believed that the Si(111)-(2×1) surface reconstruction is a buckled antiferromagnetic insulator [7] until Pandey introduced the π-bonded chain model and showed that the single-particle band theory does provide an accurate description of the electronic properties [8]. In fact, only a very few claims on Mott insulating surfaces have withstood the test of time: some room temperature (RT) saturated alkali-metal/GaAs(110) interfaces are believed to be Mott insulators [9–11]. Most recently, it was argued that the charge-density-wave phase of Pb/Ge(111) is a Mott insulator [12].

Model calculations for the two-dimensional rectangular lattice of the alkali/GaAs(110) interfaces produce an "upper Hubbard band" (UHB) and a "lower Hubbard band" (LHB), separated by a distinct energy gap when $U/W > 2$ [11]. The metal-insulator transition is predicted to occur near $U/W \approx 1.6$. From an experimental point of view, the situation is not so clear. DiNardo and co-workers have interpreted their electron energy loss spectra (EELS) of *a saturated* Cs overlayer on GaAs(110) in terms of charge transfer excitations involving the Hubbard U [9]. Nonetheless, problems exist. Inverse photoemission spectroscopy (IPES) [13] shows features that could perhaps be identified as the UHB but the LHB has not been seen in photoemission spectroscopy (PES) [13].

In this Letter, we report on momentum-resolved PES and IPES data of the K/Si(111)-$(\sqrt{3} \times \sqrt{3})R30°$-B (henceforth K/Si) interface. The interface consists of a monatomic alkali layer on top of a Si(111) surface with a boron underlayer (Fig. 1) [14]. At zero alkali coverage, the dangling bond surface states are completely empty [14]. When the alkali coverage saturates at 1/3 monolayer [15–17], the surface consists of a $(\sqrt{3} \times \sqrt{3})R30°$ arrangement of half-filled dangling bonds and, consequently, the interface should be metallic according to band theory [16]. Instead, the *single-particle* excitation spectra (PES/IPES) show two prominent features near the Fermi energy, E_F, which are identified as the Hubbard bands of a 2D Hubbard system. We analyze the spectra following Harrison's scheme of incorporating the Hubbard U into tight-binding theory [4] and discuss important implications for the electrical transport and magnetic properties.

Experiments were carried out in two different ultrahigh vacuum systems. Momentum-resolved PES data were acquired at the beam line U12B of the National Synchrotron Light Source [16]. The overall resolution of the PES spectra is $\approx$0.1 eV. Momentum-resolved IPES

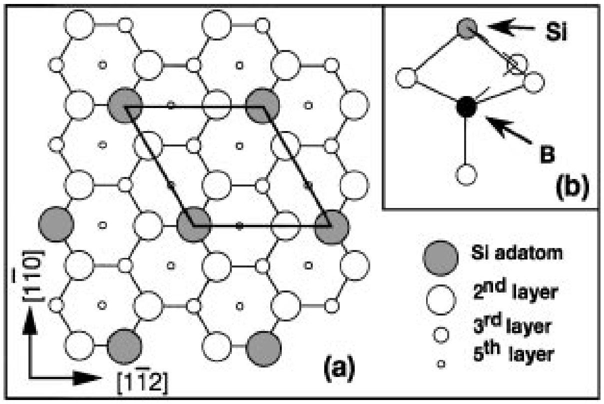

FIG. 1. Atomic geometry of K/Si(111)-($\sqrt{3} \times \sqrt{3}$)$R30°$-B (a). Shaded circles represent Si adatoms, located directly above the fivefold coordinated B atoms as shown in (b). Si adatom sites are the most likely chemisorption sites for the alkali atoms.

data were acquired at constant incident electron energy of 12.5 eV; the emitted photons were dispersed using a grating monochromator [18]. The overall energy resolution is ≈ 0.3 eV. The alkali/Si interface was produced following the procedures in Ref. [16]. The alkali coverage was monitored by measuring the work function change, $\Delta\Phi$, using an electron gun. The relationship between the work function decrease and the alkali coverage has been documented in Ref. [17]. Low energy electron diffraction (LEED) indicated that the ($\sqrt{3} \times \sqrt{3}$)$R30°$ symmetry remains preserved up to saturation coverage.

Coverage-dependent IPES and PES data of the K/Si interface were recorded at $\boldsymbol{k}_{\parallel} = 0$ [Fig. 2(a)]. The IPES data of the clean Si(111)-($\sqrt{3} \times \sqrt{3}$)$R30°$-B surface ($\Delta\Phi = 0$) show an empty state Σ at ≈ 1.1 eV above E_F. This state originates from the empty dangling bond surface state and has mixed B $2p_z$ and Si $3sp_z$ character [14]. Its band dispersion is significant: ≈ 0.6 eV [14]. With increasing K coverage, the empty state spectra from the K overlayer initially "smear out." A K-induced empty state, S_1, develops and shifts toward E_F near saturation ($\Delta\Phi = -2.9$ eV). The PES data reveal two filled states labeled B and S_2. Peak B in Fig. 2(a) is a bulk feature which shifts toward higher binding energy upon K deposition, due to band bending [15,16]. S_2 is a K-induced surface state, centered at ≈ 0.7 eV below E_F. Even though the tail of S_2 comes to within ≈ 0.1 eV of E_F, the PES data *never* show any intensity at E_F, even at saturation coverage. This suggests that S_1 and S_2 are separated by a very small energy gap, probably on the order of ≈ 0.1 eV.

The momentum dispersion of S_1 and S_2 were probed along both major symmetry directions of the ($\sqrt{3} \times \sqrt{3}$)$R30°$ surface Brillouin zone (Fig. 3). Both surface states lack significant momentum dispersion (≈ 0.2 eV), which *by definition* means that these states are *strongly localized* in real space. Near the zone boundary at $\overline{\mathrm{K}}$, another surface state, S_3, emerges. S_3 is the backbond surface state of the Si adatom which is also present at the clean surface [16]. In contrast to S_1 and S_2, S_3 does exhibit *significant dispersion.* Its persistence upon K deposition indicates that the backbonds of the Si adatoms remain intact up to saturation coverage [16] and that the saturated interface is well ordered.

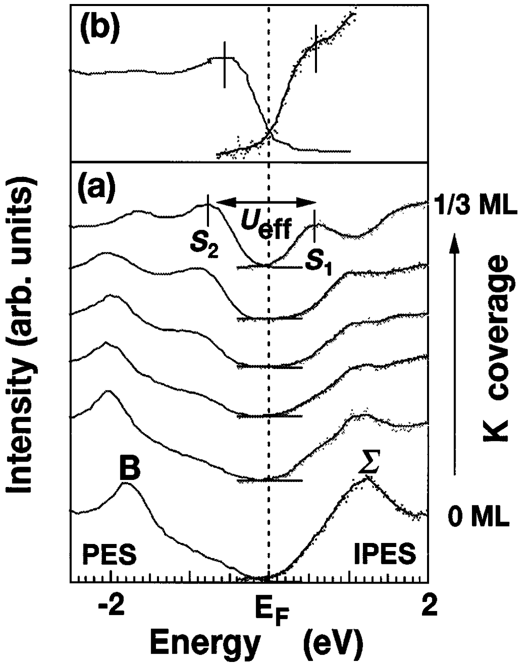

FIG. 2. (a) PES/IPES data of the K/Si(111):B interface as a function of coverage. Coverage intervals are nearly equal. Spectra were recorded at $k_{\parallel} = 0$; (b) PES/IPES data from a saturated Cs overlayer.

The clean ($\sqrt{3} \times \sqrt{3}$)$R30°$-B surface is composed of a ($\sqrt{3} \times \sqrt{3}$)$R30°$ arrangement of Si adatoms atop the T_4 sites of the (111) substrate [14]. Boron atoms are located directly beneath the Si adatoms (Fig. 1). The dangling bond orbitals of the Si adatoms are completely empty [Σ in Fig. 2(a)]. Next, the alkali atoms bond to the surface atoms without disrupting the Si-Si backbonds. This assertion is based on the facts that the backbond state S_3 and the ($\sqrt{3} \times \sqrt{3}$)$R30°$ symmetry remain intact during alkali deposition. Then, according to the single-particle picture, the addition of the alkali valence charge should shift the Fermi level well into the substrate dangling bond surface state *band* Σ, resulting in a *half-filled band at saturation coverage* (1/3 ML) [15–17]. The gradual filling of this Σ band upon K adsorption is clearly evident from the boron K-edge photoabsorption spectra (XAS) of the K/Si interface [15]. According to Ma *et al.*, XAS and Si $2p$ core level spectra indicate a large charge transfer from K to the Si-substrate dangling bond state which has become a hybrid of the Si sp^3, B $2p_z$, and K $4s$ wave functions [15]. Nonetheless, regardless of the alkali coverage, experiment never reveals any state density at E_F which indicates that correlations play a crucial role. To analyze the spectra, we use a tight-binding approach

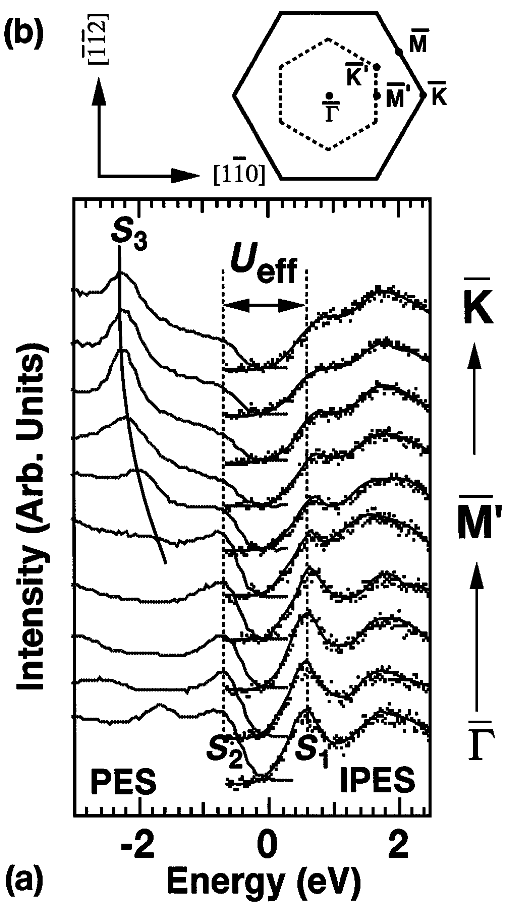

FIG. 3. (a) Momentum-resolved spectra of the K/Si(111):B interface along the $[1\bar{1}0]$ or $\overline{\Gamma\mathrm{K}}$ direction of the Si substrate; see also (b) PES data are taken from Ref. [16]. IPES data were recorded with an incident electron energy of 12.5 eV. Momentum intervals are nearly equal.

by Harrison [4] and model the saturated interface as a $(\sqrt{3} \times \sqrt{3})R30°$ lattice of half-filled dangling bonds.

The effective Coulomb repulsion, $U_{\rm eff}$, between two electrons in a Si dangling bond can be *estimated* from $U_{\rm eff} = (U - V)/\varepsilon \approx 1\text{–}2$ eV where U is the intrasite Coulomb term ($\approx$7.6 eV; Ref. [4]), V the intersite or Madelung term ($\approx$3 eV; Ref. [4]) and $\varepsilon < (1 + \varepsilon_{\rm si})/2 \approx 6$ the dielectric constant of the semi-infinite Si substrate. The hopping integral between neighboring dangling bonds on an ideally truncated Si(111) surface, t, is $\approx$0.07 eV [4]. Hence, on a $(\sqrt{3} \times \sqrt{3})R30°$ superlattice, we can safely assume that $t < 0.07$ eV, consistent with the experimental dispersion $W \approx 0.2$ eV ($W = 8t$). Hence, the Harrison criterion for a Mott insulating ground state on Si(111), $U_{\rm eff}^2 > 16t^2$, is *strongly satisfied.* Accordingly, the excitation spectrum should reveal two narrow energy bands (i.e., the ionization and affinity states) which are separated by a Hubbard gap of order $U_{\rm eff}$. Indeed, the PES/IPES data reveal two narrow bands around E_F which are now identified as the LHB and UHB of a 2D Mott-Hubbard system. The separation between the centroids of the bands is 1.3 eV, fully consistent with the above estimate of $U_{\rm eff}$. However, the *Gaussian* width [19] of the Hubbard bands ($2\sigma \approx 0.7$ to 0.8 eV) is much larger than the actual bandwidth or dispersion ($W \approx 0.2$ eV). To account for the linewidths, we take advantage of the fact that the Mott state is so well defined that we can treat the system as a two-level system (UHB/LHB).

Consider the effect of charge fluctuations δZ between neighboring dangling bond orbitals in a simple force-constant model. Setting the ground state energy to zero, the total energy of a dangling bond orbital, E_T, becomes [4]

$$E_T = C(u/d)^2 + 12(u/d)\nu_1\delta Z + U_{\rm eff}\delta Z^2, \qquad (1)$$

where u is the vertical displacement (buckling) of the Si adatom due to electron-phonon coupling, C is the "force constant" (53 eV; Ref. [20]), d is the in-plane lattice constant, and $\nu_1 = (\varepsilon_s - \varepsilon_p)/4 = -1.1$ eV [20] (ε_s and ε_p are the s and p levels of the Si atom). E_T minimizes with respect to δZ at $u = 0$ (unbuckled ground state). In essence, Eq. (1) represents the effects of electron-electron *and* electron-lattice interactions. In the electronically excited state, $\delta Z = -1$. Then Eq. (1) minimizes with respect to u when $u/d = 6\nu_1/C$, which means buckled surface. If the surface atoms remain stationary during the infinitesimal time scale of the excitation process, then the spectrum represents the Franck-Condon envelope of the *unbuckled initial state* and the *buckled final state.* For an instantaneous electron transfer or "vertical ionization," $u = 0$ so that $E_T = U_{\rm eff} = E_0 + s\hbar\omega$ where s is the number of phonons involved in the vertical Franck-Condon transition and $\hbar\omega$ the phonon frequency [21] (Fig. 4). Minimization of Eq. (1) with $\delta Z = -1$ yields $E_T = U_{\rm eff} - 36\nu_1^2/C \equiv E_0$ which equals $U_{\rm eff} - s\hbar\omega$ in the Franck-Condon picture (Fig. 4). The spectral distribution near 300 K can now be calculated from [21]

$$I(E) \propto \exp(-E^2/4k_BTs\hbar\omega), \qquad (2)$$

which is a Gaussian centered at $E_0 + s\hbar\omega = U_{\rm eff}$. The calculated linewidth ($2\sigma \approx 0.6$ eV) is close to the observed linewidths in PES/IPES ($2\sigma \approx 0.7$ to 0.8 eV). This close agreement is perhaps a little fortuitous but demonstrates that the line shapes and level splittings can be remarkably well accounted for using a simple model with well-documented parameters for ν_1 and C [20]. The surface state peaks are thus believed to represent the "Franck-Condon envelopes" of the vibrational excitations in the positive- or negative-ion final states of the PES/IPES experiment.

The large lattice relaxation or buckling in the excited state indicates that the conduction mechanism is of the polaron type. The separation between the vibrationally broadened ionization and affinity states (LHB/UHB) defines the conductivity gap ($\approx$0.1 eV) and is much smaller than $U_{\rm eff}$. Evidently, $U_{\rm eff}$ is largely compensated by the local lattice relaxation during a charge excitation. The importance of the polaron effect was previously emphasized

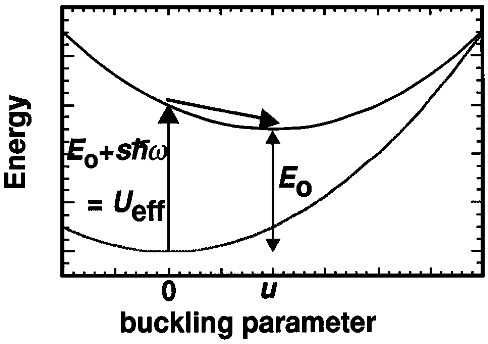

FIG. 4. Schematic Franck-Condon diagram.

in the theoretical works by Chen *et al.* [20] and by Tejedor *et al.* [22] for Si(111), and more recently by Pankratov and Scheffler for Na/GaAs(110) [10]. In the case of Na/GaAs(110), the lattice relaxation energy even overcompensates the on-site Hubbard U, leading to the formation of a bipolaron or negative U-center [10]. In the present situation, this should result in a doubling of the unit cell, i.e., $(2\sqrt{3} \times \sqrt{3})R30°$, which is not observed in LEED.

EELS spectra of K/Si [17] reveal a broad ($2\sigma \approx 0.6$ eV) but prominent loss peaked at $\approx$0.1 eV, consistent with a charge transfer excitation, Δ, on the order of U_{eff}. The present data suggest an exciton shift of $U_{\text{eff}} - \Delta \approx 0.3$ eV. Interestingly, EELS data from a *cesium* overlayer [17] exhibit a similar loss peak, but a metallic Drude tail gradually fills the gap as the coverage approaches saturation [17]. The PES/IPES spectra from the saturated Cs layer are shown in Fig. 2(b). Here, the Hubbard bands clearly cross E_F. Evidently the Cs/Si interface "metallizes" before the monolayer is completed as the vibrationally broadened Hubbard bands overlap and form a *pseudogap* near E_F. From PES/IPES [Fig. 2(b)] and EELS [17], we find $U_{\text{eff}} \approx 1.1$ eV and $\Delta \approx 1.1$ eV. The *nonmetal-metal transition* in the Cs layer is likely triggered by an electronic effect as the band dispersion of the Cs-induced state ($\approx$0.3 to 0.4 eV; Ref. [23]) is slightly larger than for K. This slight increase in band dispersion may be sufficient to close the already small conductivity gap between the vibrationally broadened Hubbard bands in Fig. 2(b).

The present study may have profound implications in the world of semiconductors and magnetism. The Mott insulating ground state implies that the surface atoms carry local magnetic moments which couple antiferromagnetically [1]. Because of the threefold lattice symmetry, however, the antiferromagnetic spin lattice is inherently "frustrated." The possibility of long-range magnetic ordering in the frustrated 2D triangular lattice antiferromagnetic Heisenberg (TLAH) system has been subject to theoretical scrutiny [24–26]. There are no materials that conform to the TLAH model and, consequently, experimental verification of the various theories has not been possible. We *speculate* that these alkali/Si interfaces present the first experimental realization of the TLAH model. Other candidates such as $NaTiO_2$ are 3D crystals with weak interlayer coupling [27].

In conclusion, we have presented experimental evidence for the correlated ground state of the K/Si interface. The polaron effect strongly *reduces* the actual conductivity gap but does not fully compensate U_{eff}. We find no evidence for a negative U-center. The present results call for the exploration of the magnetic properties of these interfaces.

We acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society for the partial support of this research. N. J. D. acknowledges the National Science Foundation, Contract No. DMR 93-13047 and DMR 91-20668. Oak Ridge National Laboratory is managed by Lockheed Martin Energy Research Corporation for the U. S. Department of Energy (DOE) under Contract No. DE-AC05-96OR22464. Brookhaven National Laboratory is funded under DOE Contract No. DE-AC02-76CH00016.

[1] For a review, see N. F. Mott, *Metal-Insulator Transitions* (Taylor and Francis, New York, 1990), 2nd ed.
[2] P. W. Anderson, Science **235**, 1196 (1987).
[3] R. W. Lof *et al.*, Phys. Rev. Lett. **68**, 3924 (1992).
[4] W. A. Harrison, Phys. Rev. B **31**, 2121 (1985).
[5] W. Beall Fowler and R. J. Elliot, Phys. Rev. B **34**, 5525 (1986).
[6] K. Takayanagi *et al.*, J. Vac. Sci. Technol. A **3**, 1502 (1985).
[7] G. A. Allan and M. Lannoo, Surf. Sci. **63**, 11 (1977).
[8] K. C. Pandey, Phys. Rev. Lett. **47**, 1913 (1981).
[9] N. J. DiNardo, T. Maeda Wong, and E. W. Plummer, Phys. Rev. Lett. **65**, 2177 (1990).
[10] O. Pankratov and M. Scheffler, Phys. Rev. Lett. **71**, 2797 (1993).
[11] F. Flores, Surf. Rev. Lett. **2**, 513 (1995).
[12] J. M. Carpinelli *et al.*, Nature (London) **383**, 398 (1996).
[13] K. O. Magnusson and B. Reihl, Phys. Rev. B **40**, 7814 (1989).
[14] E. Kaxiras *et al.*, Phys. Rev. B **41**, 1262 (1990).
[15] Y. Ma *et al.*, Phys. Rev. Lett. **65**, 2173 (1990).
[16] H. H. Weitering *et al.*, Phys. Rev. B **48**, 8119 (1993).
[17] H. H. Weitering *et al.*, Surf. Sci. **307–309**, 978 (1994).
[18] P. D. Johnson *et al.*, Rev. Sci. Instrum. **57**, 1324 (1986).
[19] 2σ is defined as th width at $1/e$ of the peak height.
[20] C. D. Chen, A. Selloni, and E. Tosatti, Phys. Rev. B **30**, 7067 (1984).
[21] B. K. Ridley, *Quantum Processes in Semiconductors* (Clarendon Press, Oxford, 1988).
[22] C. Tejedor, F. Flores, and E. Louis, J. Phys. C **19**, 543 (1986).
[23] J. Chen, Ph.D. thesis, University of Pennsylvania, 1994 (unpublished).
[24] P. Fazekas and P. W. Anderson, Philos. Mag. **30**, 423 (1974).
[25] D. A. Huse and V. Elser, Phys. Rev. Lett. **60**, 2531 (1988).
[26] G. B. Arnold and G. J. Mata, Phys. Rev. B **42**, 8638 (1990).
[27] Y. Takane and K. Nakamura, Phys. Rev. B **50**, 9589 (1994).