U Parameter of the Mott-Hubbard Insulator $6H$-SiC(0001)-$(\sqrt{3} \times \sqrt{3})R30°$: An *Ab Initio* Calculation

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The $6H$-SiC(0001)-$(\sqrt{3} \times \sqrt{3})R30°$ surface exhibits one half-filled localized dangling-bond orbital per surface unit cell. Its electronic structure can accurately be described as a Mott-Hubbard insulator. We investigate its spectrum by a spin-polarized *ab initio* quasiparticle calculation. The resulting band structure shows one occupied and one empty surface band, separated by a direct band gap of 1.95 eV. Since the band gap in the spectrum of the Hubbard model is directly given by the on-site Coulomb-interaction parameter U of the dangling-bond orbital, our results allow for a reliable determination of $U = 1.95$ eV.

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Ab initio techniques have been employed with great success to describe the electronic structure of weakly correlated materials, like semiconductors or simple metals. For more strongly correlated systems, on the contrary, like d- and f-band systems, cuprates, etc., the concepts behind available *ab initio* techniques are sometimes too limited to correctly describe the complex many-body effects. In such cases model Hamiltonians like, e.g., the Hubbard model are employed. These models, however, contain free parameters that have to be fitted, thus limiting their predictive power. Therefore, it is a great and important challenge to accurately *calculate* these parameters from first principles and to form a close link between *ab initio* and model approaches. In this paper we discuss a system in which such a link is indeed possible: the Mott-Hubbard insulator ground state of the $6H$-SiC(0001)-$(\sqrt{3} \times \sqrt{3})R30°$ surface. We present the results of a spin-polarized first-principles quasiparticle band-structure calculation which, combined with a treatment of additional correlation effects within the Hubbard model, yields the correct electronic spectrum in close agreement with experiment.

To obtain the quasiparticle band structure we employ a spin-polarized generalization of the GW approximation (GWA) for the electron self-energy [1]. Mott-Hubbard insulators (in particular d- and f-electron systems) are often described by the LDA + U approach, which can be regarded as a further approximation to the GWA (see the discussion by Anisimov *et al.* in Ref. [2]). The two approaches are thus not contradictory but they complement one another. In the present case, however, the states under consideration are not strongly localized atomic d or f states, but are surface states that are composed from valence orbitals in a complex way. This can lead to problems in the LDA + U framework [2], and the accurate determination of U is difficult (see below). We believe that the GW scheme discussed in this paper provides a more direct approach to the electronic structure of the present surface system.

Among the large variety of SiC polytypes and their surfaces, the $6H$-SiC(0001)-$(\sqrt{3} \times \sqrt{3})R30°$ surface has raised particular questions concerning its electronic structure [3–10]. The thermodynamically most favorable configuration, as resulting from local-density approximation (LDA) calculations [3–5], is given by one Si adatom per surface unit cell in the T_4 position on the surface. This structure is shown in Fig. 1 (for details, see the discussion in Ref. [3]). The Si adatoms saturate the three dangling-bond orbitals of the Si top layer atoms. The adatoms, in turn, give rise to a new p_z-like dangling-bond orbital which contains one unpaired electron per unit cell. In the single-electron picture, this one electron per unit cell leads to a half-filled surface band in the fundamental bulk band gap: the band structure is metallic. The band, as resulting from an LDA calculation, is shown in Fig. 2 by the dashed line. It disperses between 1.15 and 1.6 eV, with a bandwidth of 0.45 eV. The LDA Fermi level is at 1.3 eV. The dispersion of the band can be described approximately by a simple tight-binding picture with a rather small π-π hopping term of 0.05 eV between neighboring dangling-bond orbitals.

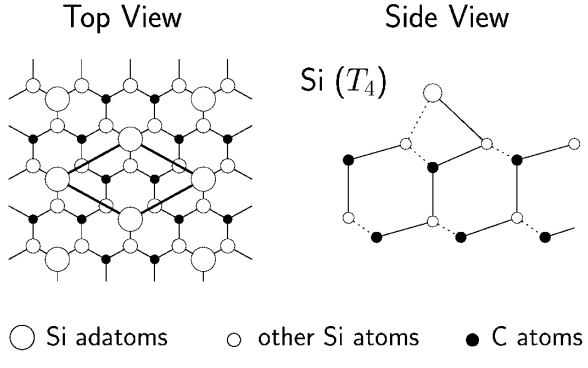

FIG. 1. Top and side view of the $6H$-SiC(0001)-$(\sqrt{3} \times \sqrt{3})$ surface (taken from Ref. [3]). Open circles (∘) denote Si atoms, full dots (•) denote C atoms. The surface is terminated by a Si layer with an additional Si adatom in T_4 position.

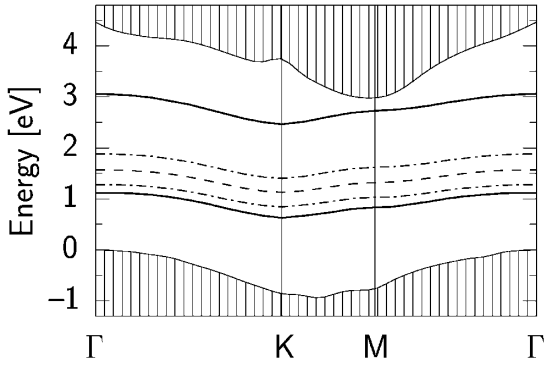

FIG. 2. Band structure of the 6*H*-SiC(0001)-($\sqrt{3} \times \sqrt{3}$) surface, calculated in LDA (– – –), LSDA (— · —), and in fully spin-polarized GWA (——).

The metallic nature of the surface band is in clear contrast to experiment. Photoemission spectroscopy [5,7,9] shows one fully occupied surface state which is about 1 eV lower than the experimental Fermi level at 2 eV. At the Fermi level, the density of states is very low, so the surface is definitely not metallic. Furthermore, inverse photoemission spectroscopy [8–10] shows the existence of an empty surface state at about 3 eV. It has already been suggested by Northrup and Neugebauer [4] and by Furthmüller *et al.* [5] that a Mott-Hubbard transition may occur at the surface, resulting in a nonmetallic ground state. This is motivated by the small hopping term between the orbitals. If the on-site Coulomb interaction of the orbital with itself (the U parameter in the Hubbard model) is significantly larger than the bandwidth, hopping of electrons between the orbitals will be suppressed. The originally metallic band, which can be filled by two electrons per unit cell, will split into *two* bands, the so-called "Hubbard bands," which are separated by U. Each of these bands can accommodate only one electron per unit cell, so that the lower Hubbard band will be completely filled and the upper one will be empty, forming a nonmetallic ground state.

The Hamiltonian of the surface states consists of three major contributions: (i) the hopping interactions t_{ij} between neighboring orbitals, (ii) the on-site interaction U of one orbital with itself, and (iii) the interaction H' of the orbitals with the rest of the crystal. [Note that two different types of correlation result from the Hamiltonian: long-range correlation effects due to H', caused by dielectric screening, and short-range on-site correlations due to U.] The usual procedure of dealing with this situation is to map the Hamiltonian onto a Hubbard model, which depends on a number of parameters [the center of mass ϵ_0 of the lower Hubbard band, the hopping terms t_{ij}, or the corresponding band dispersion $\epsilon(\mathbf{k})$, and the on-site term U], and to calculate the band structure from there on. In this mapping procedure, H' is eliminated and only enters in terms of the free parameter ϵ_0, which controls the absolute energy position of the bands. One big problem is that the actual on-site term U is strongly influenced by H' since the on-site Coulomb interaction of the orbitals is screened by the rest of the system. So once H' has been eliminated, U can only be taken as an adjustable parameter.

In our present work we suggest a reversed procedure. In a *first step,* we *calculate* the band structure by employing a highly reliable *ab initio* approach without adjustable parameters. These calculations are carried out within the GWA [1]. Its application to the present case of a Mott-Hubbard insulator requires specific attention. Depending on the spin configuration, the on-site term U can lead to complicated short-range correlation effects (see the discussion by Hubbard in Ref. [11]) that are not described by the *GW* self-energy operator. For most spin configurations, the GWA does not apply, therefore. There is, however, one spin configuration for which *the short-range correlation effects due to U are zero:* the fully spin-polarized, ferromagnetic configuration. For this case the GWA gives the correct band structure which consists of the two bands [11]

$$\epsilon_1(\mathbf{k}) = \epsilon_0 + \epsilon(\mathbf{k}) \tag{1}$$

and

$$\epsilon_2(\mathbf{k}) = \epsilon_0 + \epsilon(\mathbf{k}) + U\,, \tag{2}$$

(provided that $U \gg t_{ij}$) with $\epsilon_1(\mathbf{k})$ for the majority spin and $\epsilon_2(\mathbf{k})$ for the minority spin. From this band structure we immediately obtain the parameters ϵ_0, $\epsilon(\mathbf{k})$, and U. In a *second step,* the parameters can be used to investigate the additional short-range correlation effects due to U within the Hubbard model on top of our *GW* band-structure calculation. This allows us to evaluate the band structure for all other spin configurations in addition to the ferromagnetic one.

In order to obtain the band structure of Eqs. (1) and (2) from an *ab initio* mean-field approach it is necessary to accurately incorporate the long-range correlation and screening effects due to H' in the electronic self-energy operator. This is done in a highly reliable way by the *GW* approximation (GWA) [1]. For many systems, quasiparticle (QP) band structures in excellent agreement with experiment have been calculated within the GWA [1]. This holds especially for the fundamental band gaps that are typically obtained with an accuracy of about 0.1 eV. For the 6*H*-SiC bulk crystal we obtain a gap energy of 2.98 eV in very good agreement with the measured gap of 3.02 eV [12,14]. The GWA should be able to describe the present situation very accurately. In particular, a highly reliable value of the on-site Coulomb-interaction parameter U, which is just the direct band gap of the band structure, is obtained.

As a basis for the *GW* calculation, we first treat the system within local spin-density approximation (LSDA) to obtain the fully spin-polarized configuration. This leads already to a splitting of the former metallic LDA band into two bands separated by a direct LSDA gap of 0.6 eV (see

the dash-dotted lines in Fig. 2). Thereafter the QP corrections to the LSDA bands are calculated by a spin-polarized *GW* approach [15,16]. The resulting QP bands are shown in Fig. 2 as solid lines. Compared to the lower LSDA band, the occupied majority-spin band is shifted down to lower energies by 0.2 eV while the empty minority-spin band is shifted up to higher energies by 1.15 eV. The QP corrections depend on the wave vector $\mathbf{k}$, leading to a slight increase of the band widths from 0.45 to 0.5 eV (0.6 eV) for the occupied (empty) band. Note that the dispersion of the empty band is now stronger than that of the occupied one. This is different from the original Hubbard band structure of Eqs. (1) and (2) which gives identical dispersion for both bands. The mean direct gap between the two bands is increased by 1.35 eV due to the QP corrections and now amounts to 1.95 eV. This value of 1.95 eV is our result for the on-site-interaction parameter U of the Hubbard model. Note that we obtain indeed $U \gg t_{ij}$, which was a necessary condition for the band structure of Eqs. (1) and (2).

At the real surface, the spin configuration may not be fully polarized. In fact, within our LSDA calculation the total energy of the spin-polarized surface is nearly the same as that of the unpolarized one [17]. It can thus be expected that the spin polarization, if favorable at all, is easily broken by nonzero temperature or other perturbations, so it seems likely that the real surface is not spin polarized. The degree of spin polarization, in turn, has a dramatic effect on the electronic spectrum. For the fully spin-polarized surface the band structure is given by Eqs. (1) and (2). If the polarization is partially or totally absent, short-range correlation effects (resulting from U) arise and modify the band structure significantly. These effects are not described by the GWA but have to be discussed within the Hubbard model [11], based on the parameters ϵ_0, t_{ij}, or $\epsilon(\mathbf{k})$, and U as derived from the GWA band structure. For the specific case of zero spin polarization, i.e., the paramagnetic surface (which we consider the most realistic one), and again $U \gg t_{ij}$, the band structure is finally given by two bands [11]

$$\tilde{\epsilon}_1(\mathbf{k}) = \epsilon_0 + \frac{1}{2}\,\epsilon(\mathbf{k}) \tag{3}$$

and

$$\tilde{\epsilon}_2(\mathbf{k}) = \epsilon_0 + \frac{1}{2}\,\epsilon(\mathbf{k}) + U\,. \tag{4}$$

Compared to Eqs. (1) and (2), both bands are at the same center-of-mass position, separated by U, but the band dispersion of each band has been reduced to one half of its original value. The band structure is shown in Fig. 3. The dots and triangles in the figure denote experimental data from a combination of angle-resolved direct and inverse photoemission spectroscopy, taken by Johansson *et al.* [9]. Our calculated results agree well with the measured data.

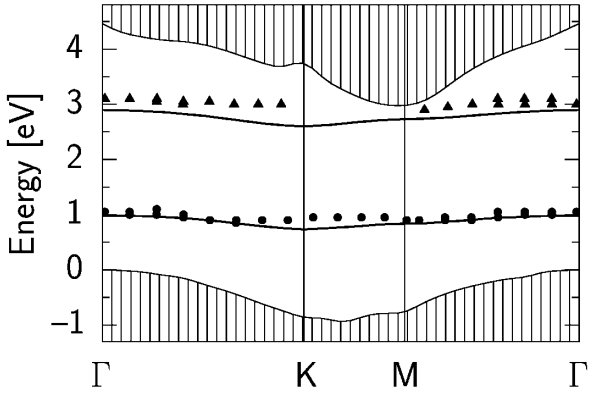

FIG. 3. Band structure of the unpolarized, paramagnetic surface, as resulting from Eqs. (3) and (4). The dots and triangles are data from direct and inverse photoemission spectroscopy, respectively, taken by Johansson *et al.* [9].

Since the direct and inverse photoemission spectrum was obtained from the same sample in the same experimental chamber, the measured band gap of $U = 2.05$ eV between the two Hubbard bands should be highly reliable.

One main point of our approach is that it allows for a direct, accurate evaluation of the U parameter. Being related to the fundamental gap energy, which is usually described very accurately by the GWA, the uncertainty of U as resulting from our band structure should be only about 0.1 eV. Alternatively, it has been suggested that U could be obtained from the change in total energy when one of the dangling-bond orbitals of the entire surface is charged with an additional or missing electron [4–6]. This has to be simulated by supercells that are artificially enlarged in the lateral dimensions, thus containing several of the orbitals. All but one of these orbitals must be saturated, e.g., by hydrogen atoms, such that the additional charge will occupy the single remaining orbital. The corresponding change in total energy can be calculated, e.g., in LDA. Within this LDA + U approach [2], Northrup and Neugebauer obtained $U \approx 1.6$ eV [4], while Furthmüller *et al.* obtained $U \approx 2.1$ eV [5]. These values for U still show significant uncertainties in the order of 0.5 eV [4]. On the one hand, they might be due to the saturation of the other orbitals which could change the properties of the remaining orbital. On the other hand, unphysical long-range Coulomb interaction effects between the orbitals may remain even for large supercells. We believe that the direct calculation of U within a spin-polarized *GW* band-structure calculation is more accurate and straightforward.

Our results are compiled in Table I, together with band-structure data obtained within the LDA + U approach [4,5] and with experimental data [5,7–9]. The center-of-mass position of the occupied, lower band (ϵ_l) is significantly lower in our data than in LDA + U because the former includes a negative QP correction. Within the LDA + U approach, it is unclear whether the energy position of the lower band should just be taken from the LDA

TABLE I. Calculated and measured band-structure data (center-of-mass energies $\epsilon_l \equiv \epsilon_0$ and $\epsilon_u \equiv \epsilon_0 + U$, band widths W_l and W_u, and direct surface band gap U) for the two surface bands l and u (in eV). The first column contains our results (cf. Fig. 3). The LDA + U results have been obtained by Northrup and Neugebauer [4] and by Furthmüller *et al.* [5]. The experimental data are from Furthmüller *et al.* [5], Johansson *et al.* [7], Themlin *et al.* [8], and Johansson *et al.* [9].

	This work	LDA + U	Expt.
Lower band: ϵ_l	0.85	1.2[a], 1.3[b]	0.95[b], 1.0[c], 0.95[e]
(Occupied) W_l	0.25	0.18[a], 0.2[b]	0.2[b], 0.2[c], 0.25[e]
Upper band: ϵ_u	2.75	2.8[a], 3.4[b]	3.4[d], 3.0[e]
(Empty) W_u	0.3	0.18[a], 0.2[b]	0.34[d], 0.2[e]
Separation U	1.95	1.6[a], 2.1[b]	2.2[c,d], 2.05[e]

[a]Ref. [4]; [b]Ref. [5]; [c]Ref. [7]; [d]Ref. [8]; [e]Ref. [9].

band. The experimental center-of-mass energy is slightly higher than in our approach but lower than indicated by LDA + U. All calculated and measured band widths (W_l) agree very well with one another. We take this as a strong indication that the assumption of zero-spin polarization, leading to the reduced band dispersion in Eqs. (3) and (4), is correct. The results for the position of the empty, upper band (ϵ_u) deviate significantly from each other. This is due to several reasons. In the calculated LDA + U data, a distinct uncertainty stems from the total energy derived determination of U (see above). In the ARIPES study by Themlin *et al.* [8], the position of the Fermi level relative to the bulk VBM was not measured but was adopted from Ref. [7], which also bears a significant uncertainty. Also for the band width of the empty band (W_u) the results scatter both in theory and in experiment. The measured data by Themlin *et al.* indicate that the band width could be larger than that of the lower band (0.34 eV as compared to 0.2 eV), which we also observe in our results (0.30 eV as compared to 0.25 eV). This effect is not described by LDA + U which gives identical band widths for both bands. Concerning the band separation U, all theoretical and experimental data agree well with one another apart from the smaller value of 1.6 eV as calculated by Northrup and Neugebauer.

In conclusion, we have performed a spin-polarized quasiparticle band-structure calculation for the 6H-SiC(0001)-$(\sqrt{3} \times \sqrt{3})R30°$ surface within the GW approximation. We have employed the most realistic structural model of a Si adatom in the T_4 position on the Si-terminated surface. The band structure of the ferromagnetic configuration consists of two nearly parallel bands with band widths of 0.5 and 0.6 eV, separated by a direct band gap of $U = 1.95$ eV. The combination of our GW band-structure results and the Hubbard model allows us to take short-range on-site correlation effects into account and to evaluate the band structure of the more realistic paramagnetic surface. This reduces the band widths of the lower and upper Hubbard bands to 0.25 and 0.3 eV, respectively. Our final results for the band structure are in good agreement with recent experimental data. Our present approach allows for an accurate calculation of the corresponding U parameter, for which we obtain a value of $U = 1.95$ eV.

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[1] L. Hedin, Phys. Rev. **139**, A796 (1965); M. S. Hybertsen and S. G. Louie, Phys. Rev. Lett. **55**, 1418 (1985); M. Rohlfing, P. Krüger, and J. Pollmann, Phys. Rev. Lett. **75**, 3489 (1995).

[2] V. I. Anisimov, F. Aryasetiawan, and A. I. Lichtenstein, J. Phys. Condens. Matter **9**, 767 (1997).

[3] M. Sabisch, P. Krüger, and J. Pollmann, Phys. Rev. B **55**, 10 561 (1997).

[4] J. E. Northrup and J. Neugebauer, Phys. Rev. B **52**, R17 001 (1995); **57**, R4230 (1998).

[5] J. Furthmüller *et al.*, Phys. Rev. B **58**, 13 712 (1998).

[6] W. Lu, P. Krüger, and J. Pollmann, in Proceedings of ICSCRM '99 (to be published).

[7] L. I. Johansson, F. Owman, and P. Martensson, Surf. Sci. **360**, L478 (1996).

[8] J.-M. Themlin *et al.*, Europhys. Lett. **39**, 61 (1997).

[9] L. S. O. Johansson, L. Duda, M. Laurenzis, M. Krieftewirth, and B. Reihl (to be published).

[10] C. Benesch and H. Merz (private communication).

[11] J. Hubbard, Proc. R. Soc. London A **276**, 238 (1963); **281**, 401 (1964).

[12] For the present case we employ a dielectric model function [see M. S. Hybertsen and S. G. Louie, Phys. Rev. B **37**, 2733 (1988)] instead of evaluating the RPA expression which would be very demanding for the $\sqrt{3} \times \sqrt{3}$ surface system. The static dielectric matrix is expanded to nonzero frequencies by using a plasmon-pole model. Both the wave functions and all two-point functions are expanded in terms of Gaussian-orbital basis functions (for details, see Ref. [13]).

[13] M. Rohlfing, P. Krüger, and J. Pollmann, Phys. Rev. B **52**, 1905 (1995).

[14] W. Choyke, D. R. Hamilton, and L. Patrick, Phys. Rev. A **133**, 1163 (1964).

[15] F. Aryasetiawan, Phys. Rev. B **46**, 13 051 (1992); F. Aryasetiawan and O. Gunnarsson, Phys. Rev. Lett. **74**, 3221 (1995); J.-L. Li, G.-M. Rignanese, E. Chang, and S. G. Louie (unpublished).

[16] Note that the dielectric screening occurring in the GWA is spin independent. This enables us to employ the model dielectric function of Ref. [12].

[17] In our calculation the energy difference between the spin-polarized and the unpolarized surface is so small that it does not allow us to determine which phase is favorable in reality.