RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 41, NUMBER 16 1 JUNE 1990

H_2O adsorption on $Bi_2Sr_2CaCu_2O_8(001)$

W. R. Flavell*
Chemistry Department, Centre for High Temperature Superconductivity, Imperial College of Science, Technology and Medicine, South Kensington, London SW7 2AY, United Kingdom

J. H. Laverty
Blackett Laboratory, Centre for High Temperature Superconductivity, Imperial College of Science, Technology and Medicine, South Kensington, London SW7 2AY, United Kingdom

D. S-L. Law
United Kingdom Science and Engineering Research Council Daresbury Laboratory, Warrington WA4 4AD, United Kingdom

R. Lindsay, C. A. Muryn, C. F. J. Flipse, G. N. Raiker, P. L. Wincott, and G. Thornton
Interdisciplinary Research Centre in Surface Science and Chemistry Department, Manchester University, Manchester M13 9PL, United Kingdom

(Received 22 February 1990)

Photoemission results show that water is physisorbed on a single-crystalline (001) face of the high-temperature superconductor $Bi_2Sr_2CaCu_2O_8$ at 90 K. A simple model of the electronic structure, in which Bi III lone-pair electrons protrude from the surface, is suggested to account for the stability of this surface in ultrahigh vacuum compared with other oxide superconductors.

All families of superconducting oxides are to some degree susceptible to atmospheric degradation reactions when in contact with air containing water vapor. In particular, it is now well established that $YBa_2Cu_3O_7$ reacts with CO_2, in a reaction which is strongly catalyzed by water vapor, to form a number of insulating products, including $BaCO_3$.[1] Although the Bi-Sr-Ca-Cu-O superconductors appear to be rather less reactive towards atmospheric gases,[2] other high-T_c superconductors appear to behave in a broadly similar manner to $YBa_2Cu_3O_7$.[3] Careful studies of the surface processes occurring during these degradation reactions are crucially important, as the atmospheric stability of the high-T_c oxides is likely to limit the scale of their technological application.

In the following we concentrate on the initial reaction of the single-crystal (001) surface of $Bi_2Sr_2CaCu_2O_8$ with water at low temperature. The (001) surface cleaves easily under ultrahigh vacuum (UHV) conditions, resulting in a surface terminated by relatively defect free, homogeneous planar Bi-O layers.[4-7] This is in contrast to other less anisotropic high-T_c materials such as $YBa_2Cu_3O_7$, where stepped surfaces may be produced.[8] Thus, it is possible to probe the intrinsic surface reactivity of this surface. We find the $Bi_2Sr_2CaCu_2O_8(001)$ surface to be extremely stable in UHV, with H_2O being physisorbed at 90 K.

Angle-resolved photoemission measurements employed the toroidal grating monochromator ($15 \leq h\nu \leq 90$ eV), VG ADES 400 instrument and low-temperature manipulator on station 6.2 at the Synchrotron Radiation Source, Daresbury Laboratory. The combined (monochromator and analyzer) energy resolution was 0.15 eV, and an analyzer entrance aperture was used to fix the angular resolution at ±2° (full width at half maximum). Contaminant-free surfaces suitable for photoemission measurements were obtained by peeling the c-axis-oriented,[7] $T_c = 84$ K single-crystal sample (SuperconiX Inc.) at room temperature using a tab technique. After removal from the spectrometer, the cleaved surface used in the present study was found to be oriented such that photoemission measurements had been carried out at about 12° from normal emission. Laue back reflection confirmed the crystallinity of the cleaved surface, although some evidence of twinning was detected.

The base pressure of the spectrometer was maintained at $\sim 3 \times 10^{-10}$ mbar, the partial pressure of H_2O being $\sim 1 \times 10^{-10}$ mbar. Exposure to H_2O was carried out using the vapor of double distilled water which was thoroughly degassed before use. Water vapor was admitted to the vacuum chamber via a leak valve, the exposure in units of Langmuirs ($1\ \mathrm{L} = 1.32 \times 10^{-6}$ mbar s) being estimated from the chamber ion gauge.

Figure 1 shows clean and water-exposed valence-band photoemission spectra of $Bi_2Sr_2CaCu_2O_8(001)$, measured at $h\nu = 33$ eV. The majority of the valence-band intensity in the clean surface spectra, which lies between 1 and 8 eV binding energy (BE), originates from strongly hybridized Cu $3d$ and O $2p$ states.[3] Weak structure at around 10–12 eV BE contains contributions from Bi $6s$ emission and Cu $3d$ satellite structure.[3] There is no evident change to the clean surface spectrum on cooling from room temperature to 90 K. Although this work is focused on the low-temperature reactivity, it is worth commenting on the room-temperature stability. Prior to cooling, the sample received an effective H_2O exposure of about 20 L at room temperature, over a period of three days inside the vacuum chamber, with similar exposures to CO and H_2. The lack of any corresponding change in the photoemission spectrum indicates the relatively unreactive nature of the $Bi_2Sr_2CaCu_2O_8$ cleavage face.

On exposure of the 90 K surface to 1 L of H_2O, marked

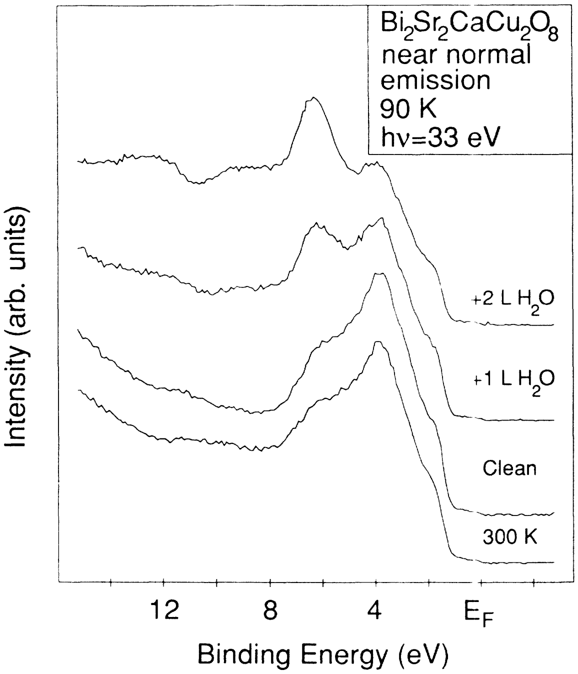

FIG. 1. Photoemission spectra of clean and water-dosed $Bi_2Sr_2CaCu_2O_8(001)$, recorded at near normal emission, using 33 eV photon energy. The substrate temperature is 90 K unless otherwise indicated and the water dose in Langmuirs (1 L $= 1.36\times10^{-6}$ mbars) is shown. The spectra are normalized to the intensity of the incident synchrotron radiation.

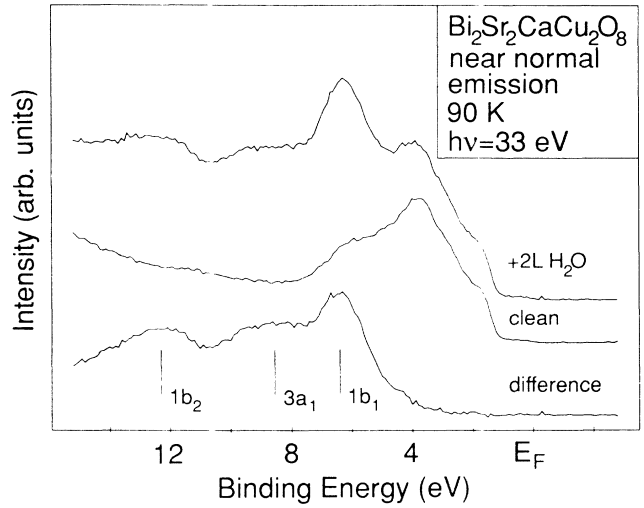

FIG. 2. Photoemission spectra of clean and water-dosed $Bi_2Sr_2CaCu_2O_8(001)$ at 90 K, recorded at near normal emission using 33 eV photon energy. The difference spectrum (2 L H_2O—clean) was obtained by normalizing the intensity away from the adsorbate-induced features. Vertical ionization energies for gas-phase water (Ref. 11) are also shown, aligned at the $1b_2$ peak positions.

changes are evident in the spectrum which are enhanced upon further exposure. The difference spectrum obtained by subtracting the 90 K clean spectrum from the spectrum obtained following a 2 L exposure is shown in Fig. 2. This reveals the presence of three well separated adsorbate-induced features with maxima at 6.5, 8.7, and 12.4 eV binding energy (the peak positions obtained from a similar analysis after 1 L exposure are identical). The appearance of three adsorbate peaks, two of which lie below the valence band of the substrate oxide is typical for nondissociative adsorption.[9] This can be seen in the spectra of $SrTiO_3(001)/H_2O$,[10] where it is possible to make a direct comparison between molecularly and dissociatively adsorbed H_2O. A comparison between the $SrTiO_3(001)/H_2O$ data and that in Fig. 2 confirms that we are indeed observing nondissociative adsorption on $Bi_2Sr_2CaCu_2O_8(001)$ at 90 K.

The three adsorbate-induced features correspond to the $1b_1$, $3a_1$, and $1b_2$ levels of H_2O, as indicated in Fig. 2, where the peak positions for gas-phase H_2O (Ref. 11) have been aligned at the $1b_2$ energy. The peak positions and their spacings relative to those for gas-phase H_2O are summarized in Table I along with data for other oxide systems where water adsorbs nondissociatively at low temperature.[9,10,12–19] A comparison of the data in Table I gives some insight into the low-temperature reactivity of H_2O with $Bi_2Sr_2CaCu_2O_8(001)$. Several general points emerge from this analysis. First, we may use the BE's of adsorbate features as a measure of the relative polarization-relaxation shift.[12] The data of Table I indicate that this shift is large for metallic substrates, as expected given the enhanced screening of the final state. For $Bi_2Sr_2CaCu_2O_8(001)$, this shift is 6.1 eV to lower-energy relative to the ionization potentials for gaseous H_2O. This is comparable with the shift observed in polycrystalline $YBa_2Cu_3O_7$,[18] and only slightly larger than the shift observed for the metallic sodium tungsten bronze, $Na_{0.7}WO_3(100)$.[17] In contrast, semiconducting oxides such as $SrTiO_3(001)$ (Refs. 9 and 10) and $SnO_2(110)$ (Ref. 14) (both having $\sim10^{17}$ carriers cm^{-3}) show a rather smaller shift. For both metallic and semiconducting substrates, with increasing exposure the polarization-relaxation shift is reduced, tending towards the values for ice (see Table I).

In the case of chemisorbed H_2O, the $3a_1$ orbital experiences a bonding shift of up to 1.3 eV (see Table I), and the extent of the $3a_1$ bonding shift may be taken as some indication of the strength of chemisorption to the surface. For those systems shown in Table I, an increasing H_2O exposure at low-temperature results in a decrease in the $3a_1$ bonding shift as a multilayer builds up. It is, therefore, interesting to note that even for 1-L exposure, the relative spacings of the levels observed on the $Bi_2Sr_2CaCu_2O_8(001)$ substrate are virtually identical to those of gaseous H_2O,[11] with an apparent $3a_1$ bonding shift small enough to be within the limits of experimental error. It is unlikely at exposures of up to 2 L that this result is attributable to multilayer formation. It is also possible however, that H_2O coverage might not be uniform and that islands of ice have condensed onto the surface. If this were the case, we would be unlikely to observe the very large shift of all the adsorbate-induced features to lower BE relative to the spectrum of ice,[13] which we commented on above; this is in itself evidence of the influence of the substrate on the adsorbate. The conclusion there-

TABLE I. Binding energies of adsorbate-induced spectral features for nondissociative water adsorption on metal and metal oxide surfaces. For comparison, values for ice and gaseous water are shown.

	Ref.	Substrate Temp. (K)	Water Exposure (L)	Binding energy (eV)				
				$1b_1$	$3a_1$	$1b_2$	$\Delta(3a_1-1b_1)$	$\Delta(1b_2-3a_1)$
Gaseous H_2O[a]	11	...	...	12.6	14.8	18.5	2.1	3.8
Solid H_2O[b]	13	...	...	8.2	...	14.4	...	...
$SrTiO_3(001)$	10	150	0.5	7.7	10.7	13.7	3.0	3.0
$SrTiO_3(001)$	9	150	2	7.6	11.0	13.8	3.4	2.8
$SrTiO_3(001)$	9	150	70	8.2	10.5	14.4	2.2	4.0
$SnO_2(110)$	14	140	10	8.0	10.2	14.1	2.2	3.9
$TiO_2(100)1\times5$	15	120	2	7.0	9.6	12.9	2.6	3.3
$TiO_2(110)$	16	160	10	~8.0	10.3	13.2	~2.3	2.9
$Na_{0.7}WO_3(100)$	17	150	1	7.0	9.0	12.9	2.0	3.9
$Na_{0.7}WO_3(100)$	17	150	4	7.3	9.4	13.4	2.1	4.0
$YBa_2Cu_3O_7$[c]	18	20,54	5-7	~6.6	...	~12.3	...	...
$Bi_2Sr_2CaCu_2O_8(001)$	d	90	1,2	6.5	8.6	12.3	2.2	3.7
Ni,Cu[c]	19	160	2	7.3	10.2	13.4	2.9	3.2
Ni,Cu[c]	19	160	5	7.7	10.0	13.8	2.3	3.8

[a] Ionization potential.

[b] The BE values were obtained using the work function of a H_2O multilayer, 3.57 eV (Ref. 10).

[c] Polycrystalline substrate.

[d] This work.

fore is that the $Bi_2Sr_2CaCu_2O_8(001)$ surface is intrinsically very unreactive towards H_2O, which is physisorbed at 90 K.

It is now well established that the double Bi-O planes of the $Bi_2Sr_2CaCu_2O_8$ structure, which are perpendicular to the *c* axis, are only weakly held together by weak bonds, and that the structure cleaves particularly easily between these planes.[5] Thus, the topmost plane of the cleaved (001) surface is expected to be a Bi-O plane.[6] In seeking an explanation for the inert character of this surface, we can draw a parallel with the reactivity of the metallic ruthenates of bismuth and lead, $Bi_2Ru_2O_7$ and $Pb_2Ru_2O_{7-y}$. These surfaces also demonstrate a rather weakly adsorbed water overlayer.[20] The inertness of the Bi- and Pb-ruthenate surfaces towards water has been tentatively attributed to the presence of Bi III and Pb II surface cations with lone-pair electrons, which cannot act as electron acceptor (Lewis acid) centers.[20] We may extrapolate this idea to the $Bi_2Sr_2CaCu_2O_8(001)$ surface, and propose that most of the surface Bi III cations have *sp*-hybrid lone pairs protruding from the surface. This would make the surface particularly inert towards water, as is observed, and would also make the topmost surface plane nonmetallic, in accordance with recent results from scanning tunneling microscopy.[6] A similar model has previously been proposed to explain the surface properties of $SnO_2(110)$ (Ref. 21) and Sb-doped SnO_2 ceramics,[22] where reduced Sn II ions at surface sites possess dangling-bond lone pairs which form a localized surface state just above the O 2*p* valence-band maximum but well within the insulating band gap. This type of model would go some way towards explaining the much higher stability of $Bi_2Sr_2CaCu_2O_8$ in UHV over $YBa_2Cu_3O_7$ (Ref. 23) and $La_{2-x}Sr_xCuO_4$.[24]

It is interesting to note the possible relevance of these results to the debate surrounding 9.5 eV BE features observed in the spectra of both Cu-based[3,23] and Bi-based[25] oxide superconductors. Both time[25] and temperature[3,23] dependence of these features has been observed. In the case of $YBa_2Cu_3O_7$, this has led to the interesting suggestion that the 9.5 eV feature is associated with adsorbed or interstitial oxygen derived from the decomposing bulk crystal as the crystal is warmed from 20 K.[23] Here we explore a perhaps more obvious possibility that a time-dependent increase in intensity at 9.5 eV may be associated with H_2O adsorption from the residual vacuum. Earlier studies of polycrystalline of $YBa_2Cu_3O_7$ (Ref. 18) and $La_{1.8}Sr_{0.2}CuO_4$ (Ref. 24) have already identified the presence of an OH derived peak at 9.0–9.4 eV BE following reaction with H_2O. Our data on single-crystal $Bi_2Sr_2CaCu_2O_8(001)$ combined with previous data on $SrTiO_3(001)$ (Ref. 10) allow us to predict that either chemisorbed H_2O or OH would give rise to a feature at around 9.0–9.5 eV BE. In this context it is significant that H_2O exposures as low as 0.1 L can modify the valence band of polycrystalline $YBa_2Cu_3O_7$.[18] Since water is one of the major residual vacuum components in a UHV system, it seems quite likely that adventitious water contamination could occur.

In conclusion, we have observed H_2O physisorption on single-crystalline $Bi_2Sr_2CaCu_2O_8(001)$ at 90 K. A surface model involving Bi III cations with lone-pair electrons is suggested to account for this inert behavior, which distinguishes it from the behavior of other high-T_c oxide systems. This model may also explain the results of recent scanning tunnel microscope measurements.[6] Our photoemission results suggest that regardless of the mode of adsorption, interaction of the surface with H_2O will contribute to the spectral intensity at about 9.5 eV BE. This implies a possible alternative origin for the 9.5 eV BE feature frequently observed in the spectra of high-T_c materials, although studies of H_2O adsorption on other single-crystalline superconductors are needed to test this suggestion.

This work was supported by the Science and Engineering Research Council (United Kingdom) with additional support from Harwell Laboratory and (to W.R.F.) from the Royal Society. We are grateful to Dr. R. G. Egdell for useful discussions, and Mr. F. Wondre of the Clarendon Laboratory, Oxford, for Laue measurements.

---

[*] Present address: Department of Chemistry, The University of Manchester Institute of Science and Technology, P.O. Box 88, Manchester M60 1QD, United Kingdom.

[1] R. G. Egdell, W. R. Flavell, and P. C. Hollamby, J. Solid State Chem. **79**, 238 (1989).

[2] H. K. Liu, S. X. Dou, A. J. Bourdillon, and C. C. Sorrell, Supercond. Sci. Technol. **1**, 194 (1988).

[3] R. G. Egdell, W. R. Flavell, and M. S. Golden, Supercond. Sci. Technol. **3**, 8 (1990).

[4] Z. X. Shen *et al.*, Phys. Rev. B **39**, 4295 (1989).

[5] S. Nakanashi *et al.*, Jpn. J. Appl. Phys. Lett. **28**, 71 (1989).

[6] M. Tanaka *et al.*, Nature (London) **339**, 691 (1989).

[7] P. A. P. Lindberg *et al.*, Appl. Phys. Lett. **53**, 2563 (1988).

[8] K. N. R. Taylor (private communication).

[9] S. Eriksen, P. D. Naylor, and R. G. Egdell, Spectrochim. Acta Part A **43**, 1535 (1987); P. D. Naylor, Pt. II thesis, University of Oxford, 1982.

[10] N. B. Brookes, F. M. Quinn, and G. Thornton, Surf. Sci. **178**, 897 (1986).

[11] K. Siegbahn, J. Electron Spectrosc. Relat. Phenom. **5**, 1 (1974).

[12] A. J. Yencha, H. Kubota, T. Fukuyama, and T. Kondow, J. Electron Spectrosc. Relat. Phenom. **23**, 431 (1981).

[13] M. J. Campbell *et al.*, J. Electron Spectrosc. Relat. Phenom. **15**, 83 (1983).

[14] W. R. Flavell, Pt. II. thesis, University of Oxford , 1983.

[15] C. A. Muryn *et al.*, J. Phys. Condens. Matter **1**, SB127 (1989).

[16] R. L. Kurtz *et al.*, Surf. Sci. **218**, 178 (1989).

[17] D. G. Aitken *et al.*, Vacuum **33**, 753 (1983); D. G. Aitken, Pt. II thesis, University of Oxford, 1983.

[18] S. L. Qui *et al.*, Phys. Rev. B **37**, 3747 (1988).

[19] D. Schmeisser *et al.*, Phys. Rev. B **27**, 3279 (1983).

[20] R. G. Egdell, J. B. Goodenough, A. Hamnett, and C. Naish, J. Chem. Soc. Faraday Trans. I **79**, 893 (1983).

[21] P. A. Cox *et al.*, Surf. Sci. **123**, 179 (1982).

[22] R. G. Egdell, W. R. Flavell, and P. J. Tavener, J. Solid State Chem. **51**, 345 (1984).

[23] A. J. Arko *et al.*, Phys. Rev. B **40**, 2268 (1989).

[24] R. L. Kurtz *et al.*, Phys. Rev. B **37**, 7936 (1988).

[25] H. Matsuyama *et al.*, Phys. Rev. B **40**, 2658 (1989).