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[1]Surface Structure of Cleaved (001) USb_2 Single Crystal Surface

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Abstract

We have achieved what we believe to be the first atomic resolution STM images for a uranium compound USb_2 taken at room temperature. The *a*, *b*, and *c* lattice parameters in the images confirm that the tetragonal USb_2 crystals cleave on the (001) basal plane as expected. Our calculations indicate a symmetric cut between Sb planes to be the most favorable cleavage plane and U atoms to be responsible for most of the density of states measured by STM. Since the spacing between Sb atoms and between U atoms is the same, STM topography only cannot unambiguously identify the surface atom species.

Keywords: USb_2, surface, DFT, STM, UHV, *f* electrons

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Introduction

The purpose of this work is to demonstrate the power of scanning tunneling microscopy (STM) techniques combined with a theoretical underpinning to determine the surface atomic structure and properties of actinide materials, such as the quasi 2-dimensional uranium dipnictide USb_2 single crystal, thereby contributing to the understanding of their surface structural and electronic properties. The members of this interesting UX_2 (X=P, As, Sb, Bi) series of compounds display dual localized and itinerant *5f* electron behavior within the same compound due to the hybridization of the *5f* orbitals with the conduction band [1]. With the exception of UO_2, which has to be studied at elevated temperature to generate enough carriers for STM imaging [2,3,4], STM techniques have not been applied successfully to the characterization of the surface atomic structure of any other single crystal actinide compound, to the best of our knowledge. However, STM has been used to a limited extent for the study of some cerium compounds [5]. Atomic structure studies by STM are limited by the ability to prepare and maintain pristine surfaces under ultra-high vacuum (UHV) conditions. This is accomplished either by in situ cleaving of the crystal of interest or by iterative exhaustive Ar^+ ion etching or laser surface ablation in order to remove surface contaminants (such as oxygen), followed by careful annealing to remove damage and relax the surface back into the crystal plane structure. STM is well known for providing extremely high resolution atomic structural and electronic information under conditions that can, combined with theoretical calculations, reveal direct local information about atomic arrangements and local density of both filled and empty states. The latter is used extensively to distinguish between contaminants, missing atoms, local charge enhancement, and buried interstitials. However, to interpret the images obtained from a surface requires a sound theoretical understanding, particularly in a heteronuclear compound, of the surface relaxation mechanism and the contribution of different species to the local density of states (LDOS). STM probes electronic properties at the atomic level and can directly provide information about the local density of filled and empty states (LDOS) states simultaneously. A STM topograph provides the local atomic arrangement and spacing of the atoms on the surface, local defect structures (e.g. steps, vacancies, and kink sites), and the presence of contaminants, all of which are averaged over when probed in photoemission studies.

The quasi two-dimensional USb_2 is an ideal test material in which to highlight the utility of the STM technique. It has a layered tetragonal structure that is easily cleaved and has been extensively studied by a number of different techniques, such as resistivity [6], Hall effect measurements [7], photoemission [8] and angle-resolved photoemission spectroscopy [9,10], de Haas-van Alphen [11-13], neutron diffraction [14], U^{238} anti-ferromagnetic nuclear magnetic resonance [15], and U^{238} Mossbauer spectroscopy [16] techniques. A great deal of information is already known about its structure and magnetic and electronic properties. Here, we provide local information about the surfaces of this interesting compound, which we find to contain a high density of defects.

Experiment

Single crystals of USb_2 were grown in Sb flux growth [17]. The crystals were prepared for STM imaging using the following procedure: the crystals were cleaved between a-b planes to obtain thin flat crystals, which were then attached to STM platens using conductive silver epoxy; a small piece of sapphire substrate was epoxied to the top surface of each crystal using Torrseal™; and a short titanium post was attached to the sapphire substrate to facilitate in situ UHV cleaving. The freshly cleaved surfaces were characterized using an Omicron UHV-STM operating under a pressure of about $5x10^{-10}$ Torr. Due to unreliable sample cleaving and the presence of surface contaminants, even on a freshly cleaved crystal, atomic resolution STM images were achieved for only two out of 14 different USb_2 samples. Imaging was carried out using cut Pt-Ir tips under typical tunneling conditions of $\pm1V$ sample bias voltage and 0.125nA tunneling current. Both filled and empty state images were taken on one of the samples to help understand the origin of the observed surface features. A freshly prepared pristine Si(001)-2x1 surface was used to calibrate the piezoelectric scanner to correct the observed atomic spacing for the USb_2 crystals. All measurements were conducted at room temperature.

USb_2 has a PbFCl or anti-Cu_2Sb (P4/nmm) structure with a = b = 0.4270 nm, c = 0.8748 nm [10] (c = 0.8741 nm, corrected value as per recent discussion with Tomasz Durakiewicz), and c/a = 2.049. In this tetragonal layered structure, it is expected to cleave between a-b planes, which have a square arrangement of atoms in the plane perpendicular to the long axis along [001]. Figure 1 shows two different resolution images collected from one of the samples. The STM images reveal that the atoms on the cleaved surface are arranged in a square pattern, as expected for the sample cleaving between a-b basal planes. The measured distance between rows of atoms in the plane, which has been corrected using measurements from a Si(100)-2x1 surface, is 0.441 ± 0.006 nm. This value is slightly larger than the published bulk value mentioned above of 0.4270 nm [10]. Even though we do not know the source of this discrepancy, this difference might be used effectively for the level of the accuracy (±0.014 nm) for the current experiment.

Although the square atomic arrangement is clearly visible, the surface contains a significant number of what appear to be missing atoms, primarily in rows corresponding to the <100> and <010> crystal directions with equal probability. The most common feature is a single atom vacancy, followed by two to three adjacent vacancies. In order to distinguish vacancies from the presence of another type of atom (e.g. contaminant or oxygen) whose DOS differs significantly from that of the majority of atoms on the surface (in this case either U or Sb), filled and empty state images were taken simultaneously (figure 2). As can be seen in figure 2, the filled and empty state images are nearly indistinguishable, suggesting that the darker features are most likely vacancies rather than differences in the DOS between atomic species. There is no significance to the approximately 45° rotation of the rows of atoms and "vacancies" from those in figure 1 since the samples were not oriented when epoxied to the STM platens. Even though the individual atoms are not as clearly visible as in figure 1, the rows of atoms and "vacancies" are aligned at approximately 90° angles, and the atomic spacing is the same as in the first sample. Unlike the crystal shown in figure 1, this area of the second sample had a nearly equal number of atoms and "vacancies" The topographic height difference between the surface atoms and the bottom of the dark features in both sets of images is 0.080 ± 0.014 nm, which is discussed below.

Calculations

We have used ab initio density functional theory (DFT) [21] to study the surface energies of various terminations of the (001) surface of USb_2. The projector augmented wave method combined with the generalized gradient approximation [22] was used to describe the U and Sb. The k-space sampling was done through the Monkhorst-Pack scheme. Valence electrons in both U and Sb atoms are treated as itinerant. The convergence of the calculations was checked to ensure an energy convergence of better than 1 meV/atom. A total of 10 layers of atoms are in the calculation supercell. For calculations of relaxation at the surfaces, the atoms for the first 3 layers were allowed to move to minimize the forces, while keeping the center 4 layers fixed, until they were smaller than 0.5×10^{-3} eV/ Å ^{3}.

USb_2 crystallizes in the PbFCl (P4/nmm) structure with U in the (0.25, 0.25, u) and Sb in the (0.75, 0.75, *v*) position, where $u = 0.280$ and $v = 0.365$ [14]. The calculated value for *a* is 0.4274 nm while holding the value of *c*/*a*, *u*, and *v* fixed at the experimental values. If we allow *u* and *v* to change while fixing the c/a ratio, the relaxed value for *u* is 0.279, which is almost identical to the experimental value of 0.280. The relaxed *v* value is 0.359, which is again very close to the experimental value of 0.365. Overall, the agreement with experiment is very good. The anti-ferromagnetic calculations of the bulk do confirm the magnetic moment arrangement that has been observed in other experiments [15]. There are no significant differences in the energy and structural properties between the results of anti-ferromagnetic and nonmagnetic calculations. There are many possible configurations for the magnetic moments in the actinides [23]. Here we only consider nonmagnetic, ferromagnetic and antiferro magnetic solutions. We also performed relativistic calculations with spin-orbit interactions explicitly included and found that the cleavage energies and structural properties are only slightly modified and the results for the fracture energies from these spin-orbit calculations are presented in Table 2. Therefore, for simplicity, we present mostly the nonmagnetic calculations for the surface studies below.

For the (001) surface of USb_2, there are several possible surface terminations when the crystal is cleaved, as illustrated in Figure 3, where we show there are 5 possible cuts along the (001) plane at various z positions that will yield surfaces with different chemistries (Table 1). There are 5 possible cuts: cut1 is between layer 1 and 2; cut2 is between layer 2 and 3; cut3 is between layer 3 and 4; cut4 is between layer 4 and 5; and cut5 is between layer 5 and 6. Because there is mirror symmetry along the z direction, cut5 and cut1 are the same, and cut4 and cut2 are the same. There are only 3 distinct cuts with regard to surface chemistry and structure. These cuts are cut1 (with a layer spacing of 0.244 nm between Sb and U layers), cut2 (with a layer spacing of 0.070 nm between of U and Sb) and cut3 (with a layer spacing of 0.244 nm between U and Sb).

We have calculated the fracture energy (F), in mJ/m^2, and missing bonds per area (M), (per unit surface area of 0.4274 nm x0.4274 nm) of these cuts and tabulated them in Table 2. The fracture energies for these three cuts are quite different. The lowest energy cut is cut3 at 1179 (or 1186 in spin-orbit calculations) mJ/m^2, while the other two cuts are about 2 and 4 times larger in energy. These drastic differences in fracture energies are much larger than observed in the cases of $BaTiO_3$, $SrTiO_3$ and $CaTiO_3$ perovskites or for metals [18-20]. Judging only from the number of the missing bonds, one would expect that the cut3 process should yield the lowest energy surfaces, in agreement with our calculations. If the fracture process on (001) USb_2 is determined solely by the fracture energy, then the most likely cleaving surface will be the cut3 surface, with the lowest fracture energy of 1179 (or 1186 in spin-orbit calculations) mJ/m^2. The cut3 process will create two identical surfaces for the two parts that will be created. All these surfaces will terminate with a pure Sb layer on the surface, an underlying second layer of U atoms 0.070 nm below it, and a 3rd layer of Sb atoms separated from the U layer by 0.244 nm. This is followed by another layer of U atoms separated from the third layer by 0.244 nm.

With cut3 termination, we allowed the atoms of the top three layers to relax to the lowest energy with zero forces. We found that there were no lateral relaxations, as expected from the symmetry consideration. However, the vertical relaxation was significant. The 1st -2nd layer spacing changed from 0.070 nm to 0.081 nm. This represents an outward expansion of the first layer of +15.7%, which is much larger than the ~1% change observed in fcc (111) or hcp (0001) surfaces [19]. It would be very informative to do surface structure experiments by LEED or ion scattering experiments to pin down the exact position of the atoms, which will help us understand how U and Sb atoms interact on the surface of USb_2. The 2nd -3rd layer spacing contracts from 0.244 nm to 0.238 nm (-2.5% contraction), which is the opposite of the 1st layer expansion, as one would expect from the charge compensation effects of next layers. The 3rd -4th layer spacing goes from 0.244 nm to 0.243 nm (-0.4% contraction) as the oscillation of these relaxations decays into the bulk [20].

In addition to the structural studies, we also performed studies of the charge transfer between atoms to explore the electronic interactions and properties in this compound and to help interpret the STM images. We calculated the LDOS on each atom and sorted it into contributions from different orbitals. By summing the charge within a cutoff radius, we can calculate the approximate charge transfer between atoms. We found that in the bulk each U atom donates about 1 full electron and each Sb atom absorbs 0.5 electrons. The DOS at the Fermi energy is dominated by the 5*f* electrons of U by 20 to 1 when compared to Sb contributions.

The LDOS results calculated for U and Sb at the Fermi energy for the relaxed (001) surface (cut3) are shown in Fig. 4. The U/Sb ratio of LDOS at the Fermi energy is 29 to 1, indicating that the U atoms are responsible for the vast majority of the surface charge. Most of that signal is from the 5*f* electrons of U, even though only about ~3 5*f* electrons are present in a U atom (Fig. 4(a)). The much smaller contribution from Sb comes mainly from its d orbitals (Fig. 4(b)).

Discussion

A comparison of the lattice parameter along the a-axis from the STM data to the published bulk value (and with the calculations) differs from the expected value by about 3%. Since we didn't expect much lateral relaxation of the atomic positions from the calculations, and the difference is outside the STM spatial resolution accuracy, which was calibrated against the known spacing on the Si(100)-2x1 surface, we have no explanation for the discrepancy between our measurements and our calculations at this time. Further measurements will be needed to account for this discrepancy.

In contrast to the discrepancy in the lateral spacing, the measured vertical layer spacing between the top surface and the layer below (0.080 nm) is very close to the value obtained from the calculated relaxed vertical layer spacing (0.081 nm), assuming cut3. One caution: the STM topographical data is related to the LDOS, so an accurate vertical dimension is achieved primarily from pristine homonuclear surfaces. Here the top surface is predicted to consist of Sb atoms with the second layer consisting of U atoms, which are offset from the Sb atoms by $a/2$ rather than resting directly below the missing atom positions. Although this situation makes interpretation of the STM vertical dimension problematic, we can expect the measured vertical dimension to be of the right order of magnitude.

The bond breaking energy calculations above point to a top surface consisting only of Sb atoms, but the charge calculations suggest that U atoms primarily contribute to the STM LDOS filled state maps, as much as over 29 to 1 for the relaxed surface. In effect, the STM sees almost exclusively the U atoms. Since the closed-loop filled and empty state images are nearly identical in structure intensity and there are no obvious systematic displacement of features, it appears that the STM sees the same atoms in both cases. Further calculations are needed to confirm that the LDOS for filled and empty states are similar. In addition, this observation supports the interpretation that the dark features in the images are atomic vacancies. This interpretation encounters one difficulty with the energy argument, because the above process will require the surfaces with cut3, which have the lowest fracture energy, to branch into cut2 terminations, which have the highest fracture energy. This particular cut is less energetically favorable, yet there are many black spots observed in our experiments (Figs. 1 and 2). One plausible explanation for the significant number of missing atoms from surfaces is that these vacancies were formed during crystal growth and that the reduced number of atoms and bonds weakens the bonding between those particular defected layers and is not associated with the higher energy cut2 fractures.

In conclusion, we have achieved what we believe to be the first atomic resolution STM images for a uranium compound taken at room temperature. The a, b, and c lattice parameters in the images confirm that the USb_2 crystals cleave on the (001) basal plane, as expected from our calculations. Further, our calculations indicate a symmetric cut between Sb planes to be the most favorable cleavage plane and that U atoms are responsible for the majority of the DOS signal measured by STM. Since the spacing between Sb atoms and between U atoms is the same, STM topography cannot unambiguously identify the surface atom species.

Acknowledgments

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Tables:

Table 1. Possible a-b layer terminations of surface after cleaving with spacing to the next layer.

Layer	Z(nm)	Species	spacing (to next layer, nm)	spacing with relaxed u,v
1	0.0	Sb(2)*	0.245	0.244
2	0.245	U	0.074	0.070
3	0.319	Sb	0.236	0.246
4	0.555	Sb	0.074	0.070
5	0.629	U	0.245	0.244
6	0.874	Sb(2)	(same as layer 1)	(same as layer 1)

* Sb(2) indicates that there are 2 Sb atoms in the layer.

Table 2. Calculated fracture energies without and with spin-orbit (s-o) interactions required to cleave along the three possible distinct layers in the crystal.

System	F (mJ/m^2)	F (s-o) (mJ/m^2)	M (missing bonds)
Cut1	2499	2186	4 U-Sb bonds at 0.325 nm
Cut2	4953	4441	5 U-Sb bonds (1 at 0.310, 4 at 0.311 nm)
Cut3	1179	1186	2 U-Sb bonds at 0.310 nm

Figure captions:

Figure 1. STM empty state images (a) and (b) taken from a freshly cleaved USb_2 single crystal sample. Note the large number of what appear to be missing atoms. Images were taken at $V_{sample} = 1V$, $I = 125$ pA.

Figure 2. STM empty ((a) - $V_{sample} = +1V$) and filled ((b) - $V_{sample} = -1V$) state images taken simultaneously on the second USb_2 sample. Both images were taken with 150 pA tunneling current. The number of apparent "vacancies" was approximately equal to half of the surface atomic sites. The crystal axes of this crystal appear to be rotated about 45°C relative to the previous sample's axes.

Figure 3. USb_2 crystal structure showing the potential cleavage planes. The most favorable cut (cut3) is boxed.

Fig. 4. LDOS for the relaxed (001) surface (cut3) of USb_2 (a) from U atom and (b) from Sb atom at the surface. The Fermi energy is at 0 eV.

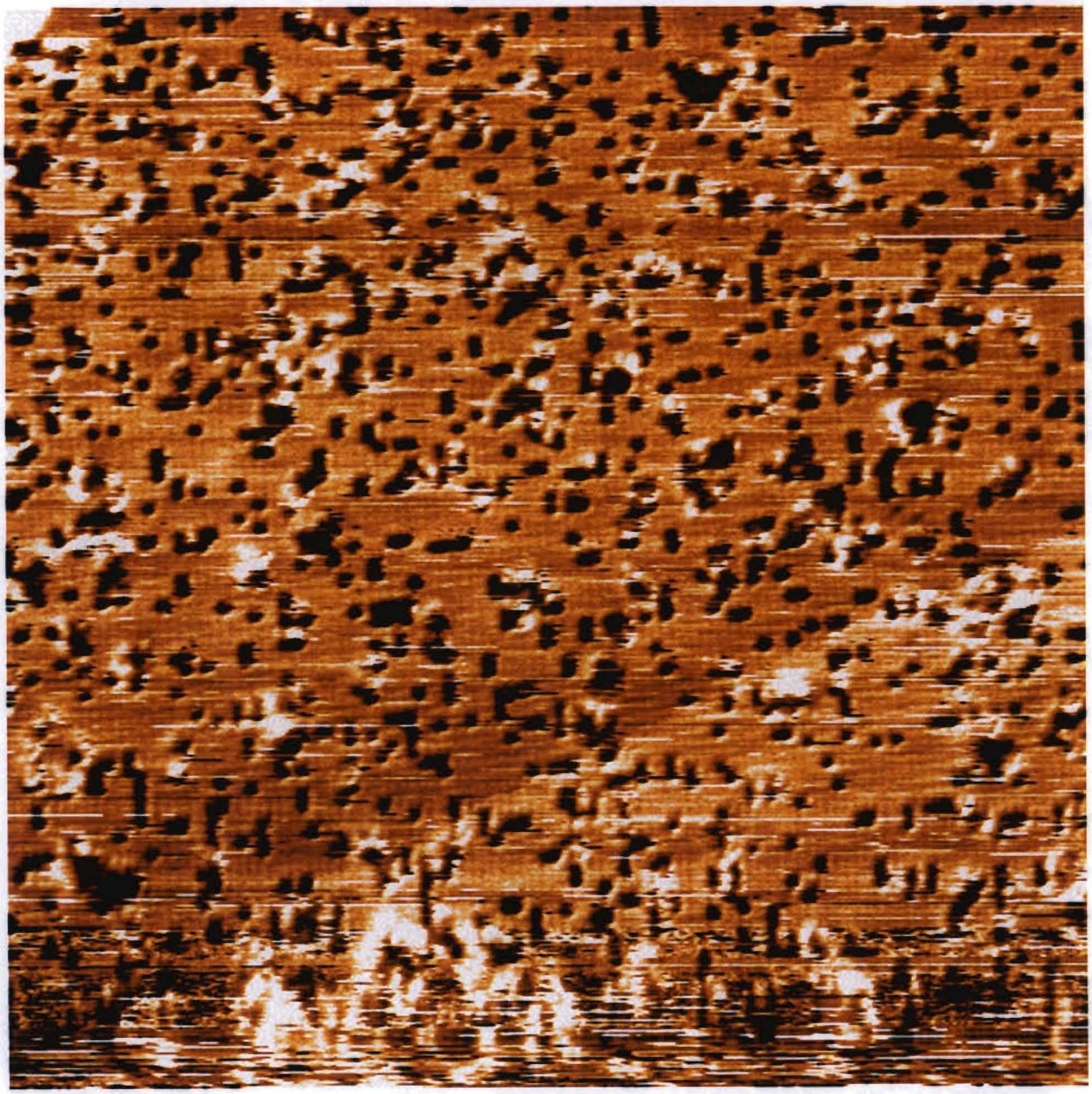

Fig. 1(a)

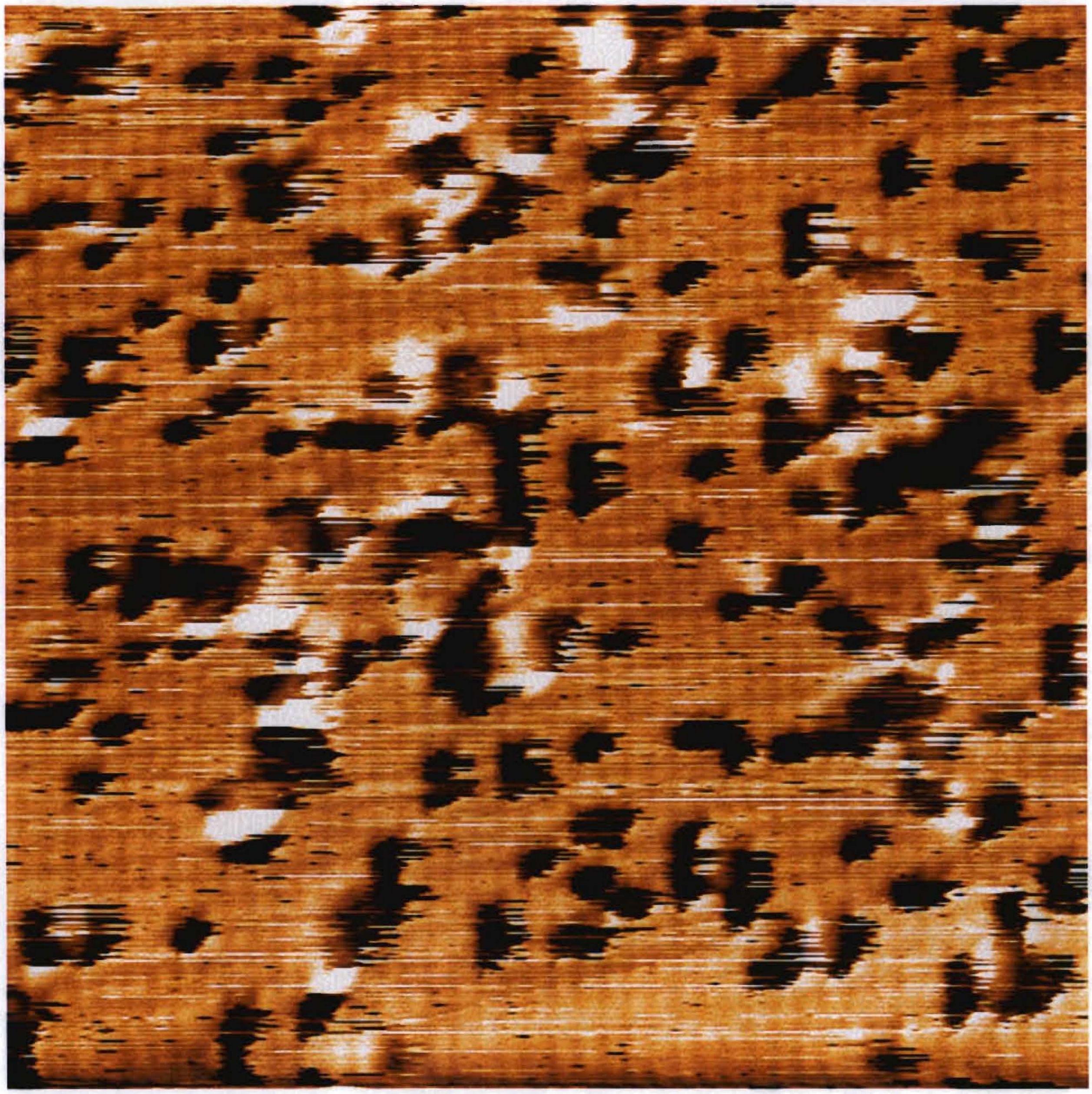

Fig. 1(b)

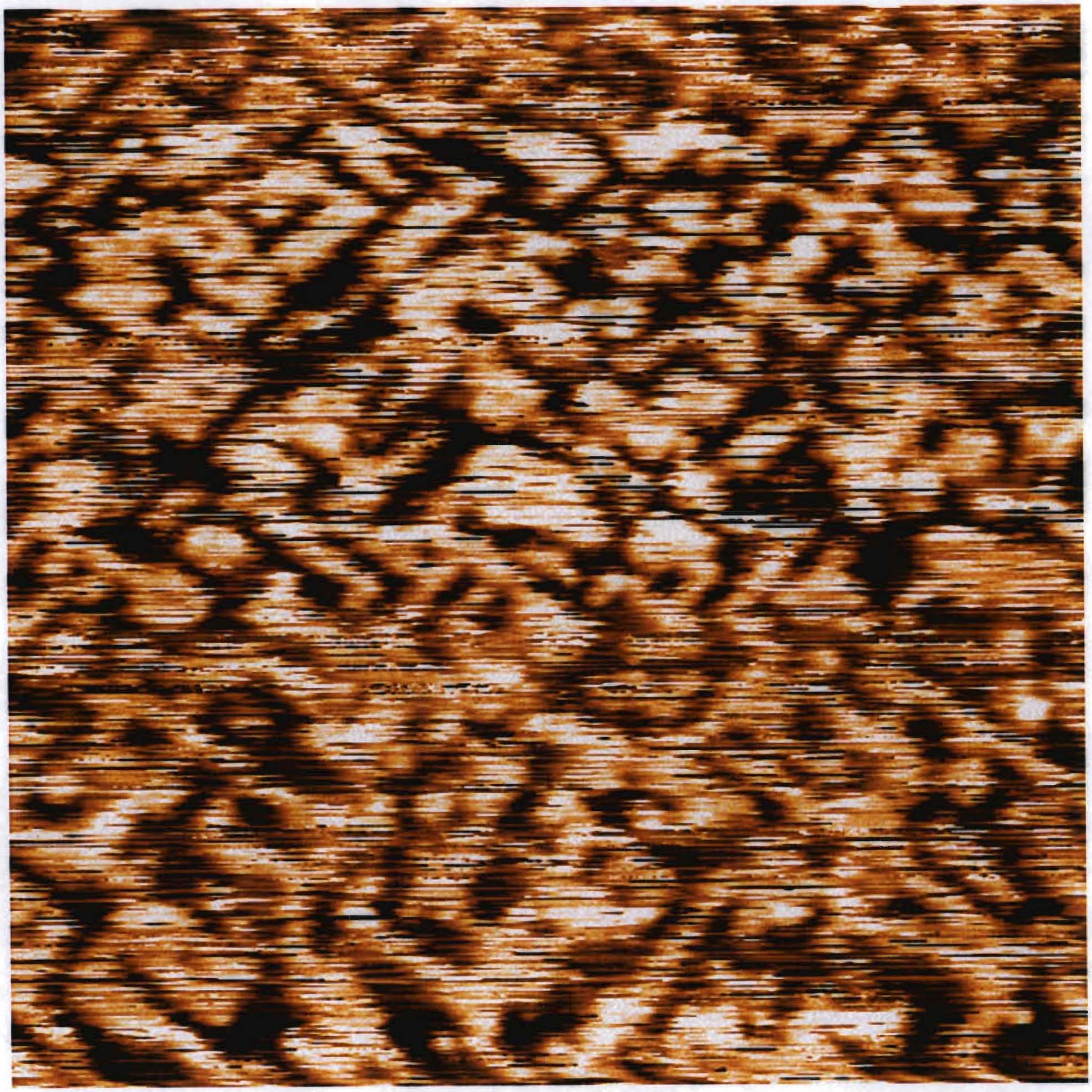

Fig. 2(a)

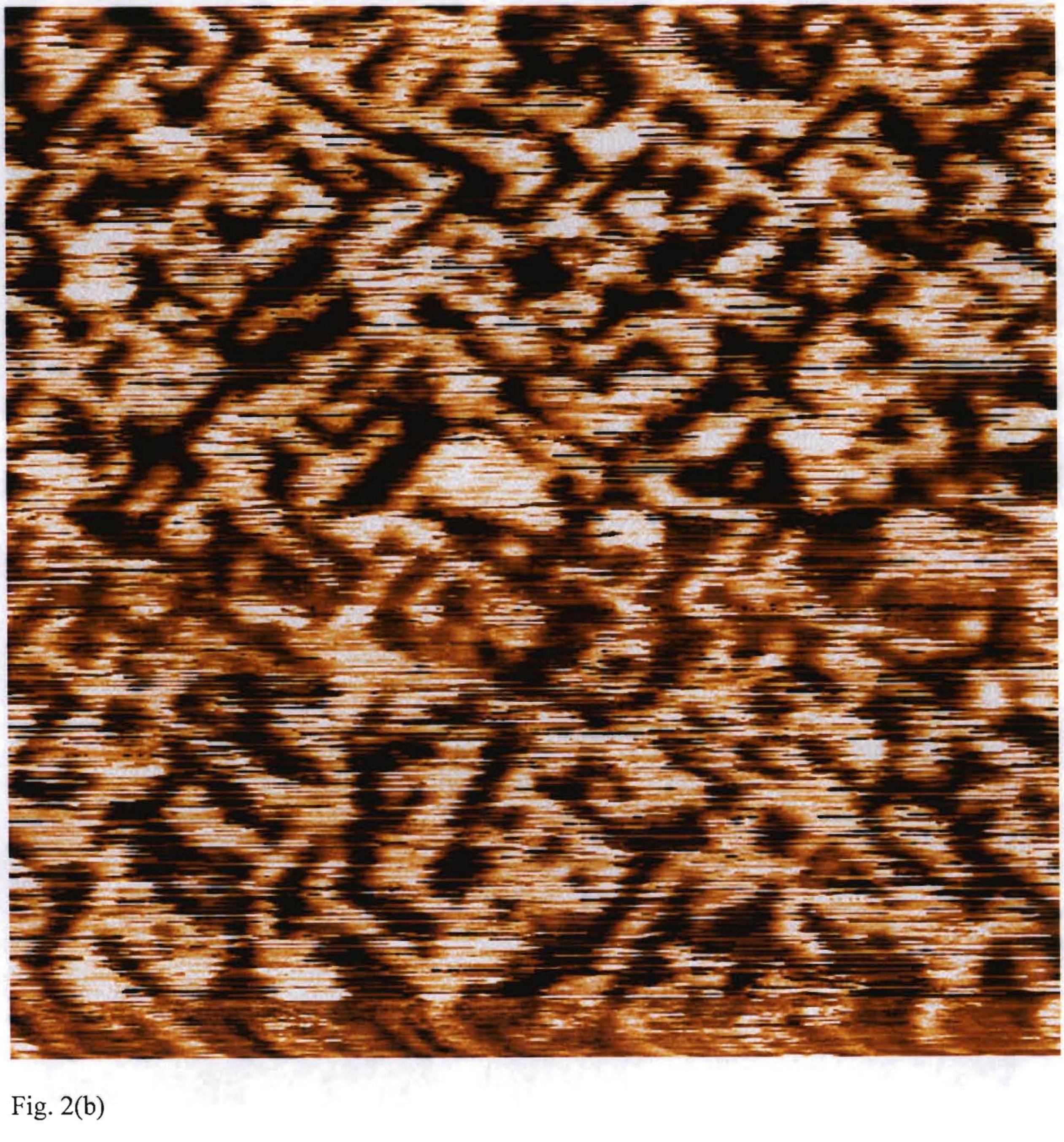

Fig. 2(b)

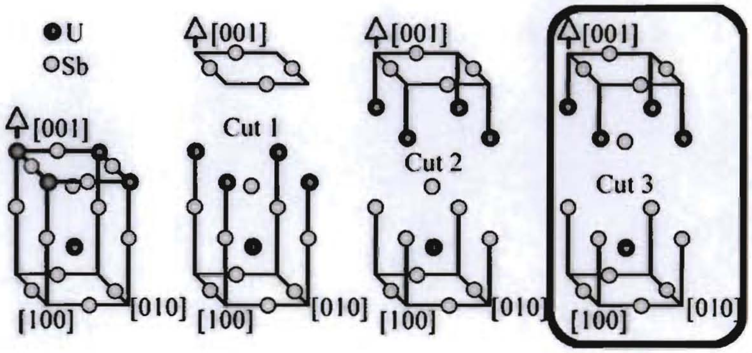

Fig. 3

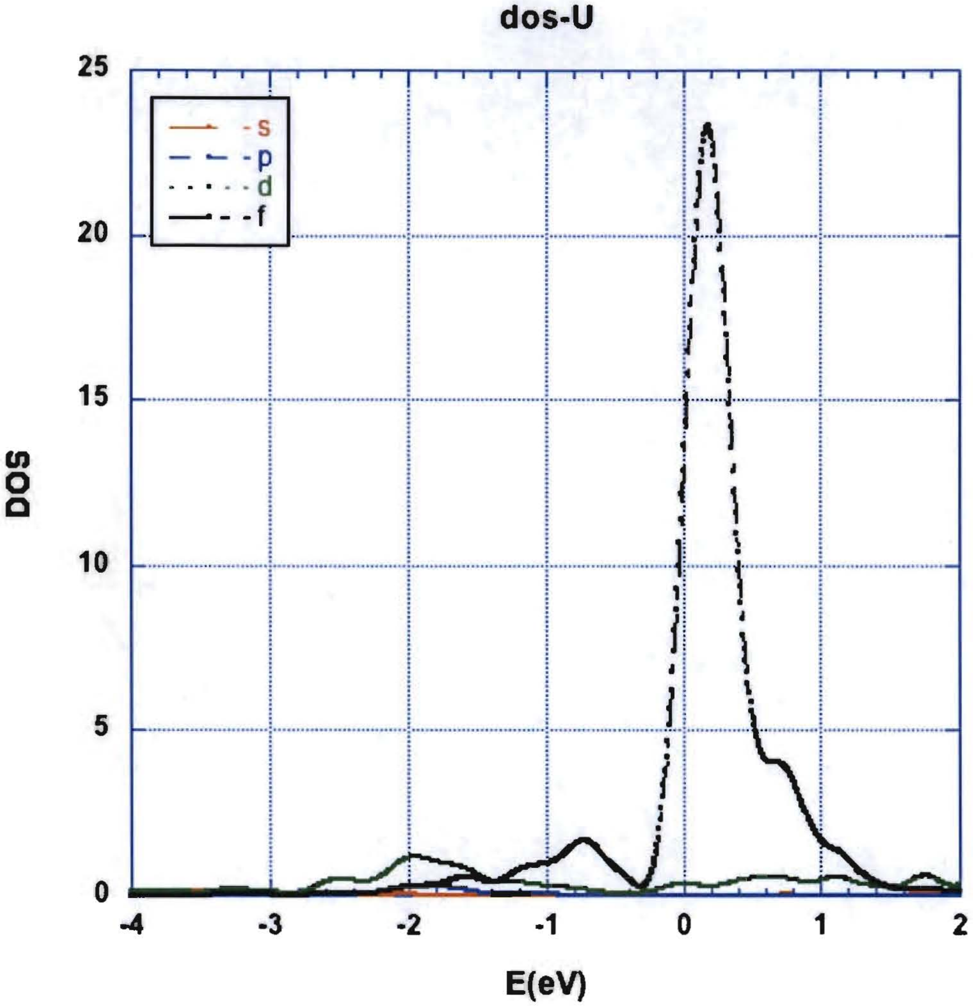

Fig. 4(a)

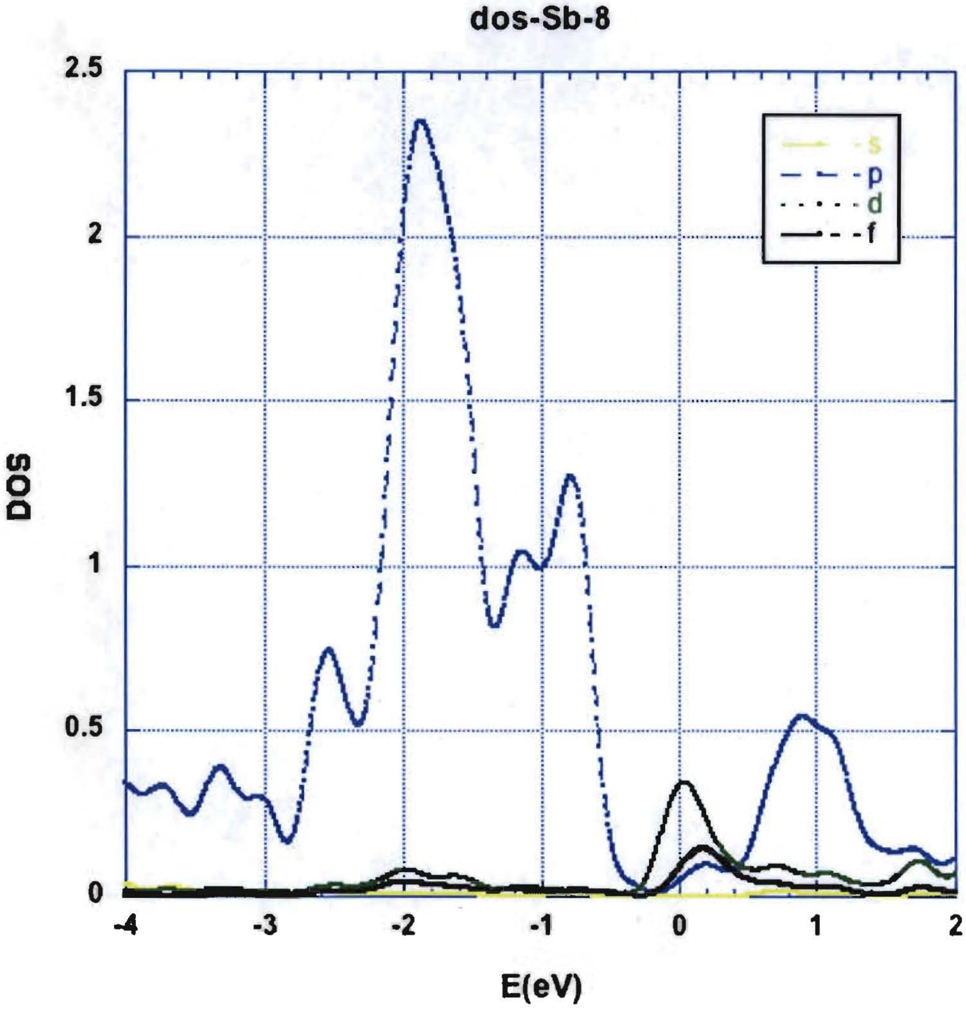

Fig. 4(b)