

## Scanning Tunneling Microscopy of Stannite and Hematite\*

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The application of scanning tunneling microscopy (STM) to the study of mineral surface was started in 1988. When STM was just invented, it can only be operated in vacuum. But by efforts of scientists in various countries, STM images down to atomic-resolution can already be obtained in air, at room temperature now. This is really a big progress in STM science. But because of the severe demands of STM for the samples, up to now, STM study has been restricted to only a few minerals which developed perfect cleavages<sup>[1,2]</sup>. In order to enlarge the mineral sample range for STM, after having experimented on molybdenite and galena<sup>[1]</sup>, with great success we apply STM to the study of stannite and hematite, which have respectively poor cleavages and only partings.

### 1 Samples and Experiments

The stannite ( $\text{Cu}_2\text{FeSnS}_4$ ) used in this study, deep grey in color with two groups of poor cleavages came from Dongchuan, Yunnan Province, China. The hematite ( $\text{Fe}_2\text{O}_3$ ), iron grey with no cleavage but two groups of partings,  $\{0001\}$  and  $\{10\bar{1}1\}$ , came from Changning, Hunan Province, China.

The experiments were performed in air at room temperature, on CSTM-9000 type STM, manufactured by the Institute of Chemistry, Academia Sinica. The tip (tungsten wire 0.5 mm in diameter) was prepared by electrochemical corrosion in 1.5 mol/l KOH solution.

### 2 Results and Discussion

Figures 1 and 2 are the atomic-scale STM images of stannite obtained with negative and positive  $V_{\text{bias}}$  respectively. Because the two cleavage groups of stannite cannot be distinguished by the eye and STM itself does not have the ability to make distinctions between different kinds of atoms, we have to decide which group of cleavage have been observed and which kind of atom was displayed by analyzing Fig. 1 and Fig. 2 combined with the crystal structure of stannite carefully.

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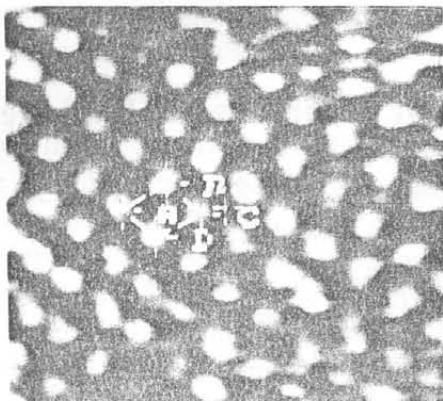


Fig.1. Atomic-resolution STM image of stannite (110) surface.

$V_{\text{bias}} = -21 \text{ mV}$ ,  $I_{\text{ref}} = 0.89 \text{ nA}$ .



Fig.2. Atomic-resolution STM image of stannite (110) surface.

$V_{\text{bias}} = 20 \text{ mV}$ ,  $I_{\text{ref}} = 0.7 \text{ nA}$ .

Stannite is of chalcopyrite type structure, tetragonal system, with  $a_0 = 5.47 \text{ \AA}$ ,  $b_0 = 10.747 \text{ \AA}$ <sup>[3]</sup>. Fig.3 is the projection of stannite crystal structure on its (001) plane. If Cu, Fe and Sn atoms are represented by the same symbol, the different kinds of symbols in Fig.3 will indicate atom-layers at different heights along (001). There are three kinds of symbols totally. All of them are arranged in square patterns and their unit cells are of the size of  $3.87 \text{ \AA}$  ( $a$ ,  $b$ ,  $c$  in Fig.3). In other words, the STM image which shows simultaneously Cu, Fe and Sn atoms has the same pattern and the same interatomic distances as the image which shows S atoms only. If only one of the three kinds of Cu, Fe and Sn atoms was displayed, the displayed atoms should also be arranged in a square pattern, but with a larger unit cell,  $5.47 \text{ \AA}$  ( $d$ ,  $f$  in Fig.3). S will not appear in the image which shows Cu, Fe and Sn atoms in (001) direction because they are in different atom-layers. But in (110) direction, it is possible to observe S and Cu, Fe, Sn at the same time, as we can see in Fig.4. Fig.4 is the schematic

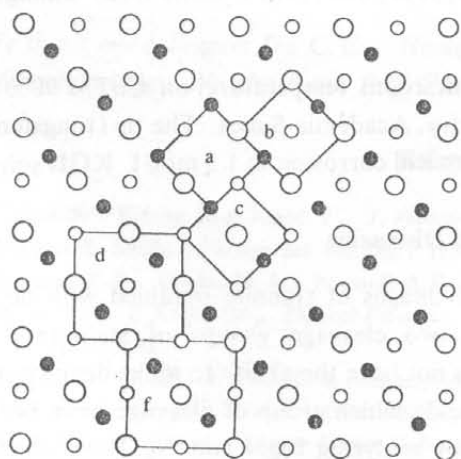


Fig.3. The projection of stannite structure along its (001) direction. The different symbols represent different atom-layers along (001).

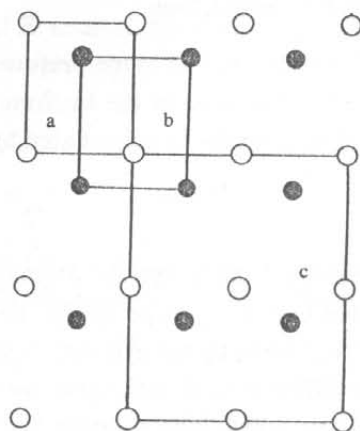


Fig.4. The schematic diagram of (110) plane of stannite structure. If one kind of symbol represents S, another represents Cu, Fe and Sn.

diagram of (110) plane of stannite structure, in which one kind of symbol indicates S and another indicates Cu, Fe and Sn. When both S and Cu, Fe, Sn atoms come out in the same image, there will be one peak at the position  $(1/4, 1/2)$  of each unit cell, as in Fig. 4. Obviously, Fig. 1 and Fig. 2 are not the case. If only S or Cu+Fe+Sn were showed, the peaks should be arranged in an oblique pattern, with a unit cell  $a, 3.87 \text{ \AA}, b, 5.37 \text{ \AA}$  ( $a, b$  in Fig. 4). If only one of Cu, Fe and Sn was displayed, the unit cell of the pattern would be three times that of  $a$  and  $b$ , like  $c$  in Fig. 4. Fig. 1 and Fig. 2 are not the case. The measured interatomic distances in both Fig. 1 and Fig. 2 are approximately  $a = 4.1 \text{ \AA}, b = 5.3 \text{ \AA}$ . So we are inclined to think that Fig. 1 and Fig. 2 are the atomic structure of stannite (110) plane, in which only S or Cu+Fe+Sn are displayed. According to the result of galena<sup>[1,2]</sup>, atoms in Fig. 1 are most likely S and atoms in Fig. 2 are probably Cu, Fe and Sn. The twisting of the patterns in Fig. 1 and Fig. 2 is caused by the obliqueness of X and Y scanning.

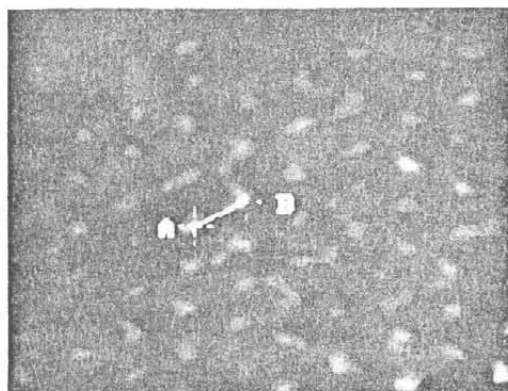


Fig. 5. Atomic-resolution STM image of hematite parting surface.  $V_{\text{bias}} = -22 \text{ mV}, F_{\text{ref}} = 0.88 \text{ nA}$ .

Fig. 5 is the STM image of hematite. Because of the same reason as for stannite, we have to decide again which parting,  $\{0001\}$  or  $\{10\bar{1}1\}$ , we have imaged.

Hematite is of the corundum type structure, trigonal system, with  $a_0 = 5.039 \text{ \AA}, c_0 = 13.76 \text{ \AA}, Z = 6$ .  $\text{O}^{2-}$  is packed in the closest way. The pack layer is perpendicular to the three-fold axis.  $\text{Fe}^{3+}$  filled  $2/3$  of the octohedral vacancies<sup>[3]</sup>. It is clear that Fe and O are in different planes both in  $\{0001\}$  and  $\{10\bar{1}1\}$  directions. So it is impossible to image Fe and O at the same time. Accord-

ing to the crystal structure of hematite, O atoms are arranged at the vertices of a set of equilateral triangles of a hexagonal net in  $\{0001\}$  direction. But the arrangement of Fe is a little different. One reason is that only two out of three octahedral sites are filled with Fe atoms (this makes Fe group in pairs), and another reason is that one member of each Fe pair shares a face with an Fe octahedron in the next layer, and the local atomic attractive and repulsive forces make the octahedron distorted. These result in an Fe pattern similar to that of O but the Fe-Fe distance is  $\sqrt{3}$  times of O-O distance (Fig. 6). In  $\{10\bar{1}1\}$  direction, O is arranged at the vertices of isosceles triangles (Fig. 7) and Fe is arranged in a similar way. But the isosceles triangle of Fe is much larger than that of O. If the radius of O is  $1.4 \text{ \AA}$ , the O-O and Fe-Fe distances in Fig. 6 will be  $2.8 \text{ \AA}$  and  $4.9 \text{ \AA}$  respectively, and the size of the isosceles triangles in Fig. 7 will be  $5.4 \text{ \AA} \times 4.9 \text{ \AA}$ . Taking the image twisting (as in Fig. 1 and Fig. 2) and the measurement errors into consideration, we can see easily that Fig. 5 matches well with the situation when Fe is displayed in  $\{0001\}$  direction or when O is displayed in  $\{10\bar{1}1\}$  direction. But more work, such as LEED, has to be done before we can make further distinctions.

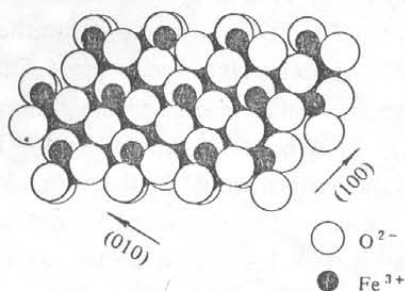


Fig.6. The arrangement of O and Fe atoms of hematite in  $\{0001\}$  direction.

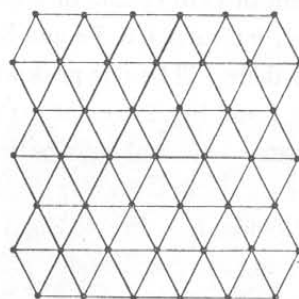


Fig.7. The arrangement of O atoms of hematite in  $\{10\bar{1}1\}$  direction.

### 3 Conclusions

Figures 1 and 2 are the first atomic-resolution STM images of stannite, which developed only poor cleavages, in the world. This result demonstrates that STM can also be used to study rough surfaces of some minerals. For hematite, Michael<sup>[2]</sup>, Eggleston<sup>[5]</sup> and Patricia<sup>[6]</sup> have already studied its  $\{0001\}$  surface, but nobody has ever studied its  $\{10\bar{1}1\}$  surface. The experiments by Michael and by Eggleston showed that Fe is displayed when  $V_{\text{bias}}$  is positive and O is displayed when  $V_{\text{bias}}$  is negative. So atoms in Fig. 5 are most likely O, and the surface we studied is probably  $\{10\bar{1}1\}$ . But some experiments have also demonstrated that variation of sample bias voltage allows for imaging different kinds of atoms. And there is a big difference between our bias ( $-22$  mV) and that of Michael ( $+1100$  mV) and Eggleston ( $-300$  mV). This brings some uncertainties in our peak-defining. In addition, STM experiments of minerals are complicated by the impurities in their compositions. The impurities not only affect the Fermi level of minerals, but sometimes even change their semiconductor type.

This study showed again that STM is a powerful tool in mineralogy study, and its potential is far from being brought into full play.

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