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QUASI-KINEMATIC LOW-ENERGY ELECTRON DIFFRACTION AND ITS LATEST APPLICATIONS*

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In order to determine the structure of complex and/or stepped surfaces that are very difficult to or even beyond the capability of the full dynamic low-energy electron diffraction calculations, recently we have proposed the quasi-kinematic low-energy electron diffraction (QKLEED) approach and employed it to solve the structure of some important surfaces such as Si(111)-($\sqrt{3}\times\sqrt{3}$)$R30°$-Al and Si(111)-($\sqrt{3}\times\sqrt{3}$)$R30°$-Ag. In the present paper, following the highlights of QKLEED we give the latest application of it, i.e., the structural determination of the *Si*(111)-($\sqrt{3}\times\sqrt{3}$)$R30°$-Au, Si(111)-($\sqrt{3}\times\sqrt{3}$)$R30°$-Sn, and *Pd*(001)-c(2 × 2)-Mn surfaces.

PACC: 6820

I. INTRODUCTION AND THE QKLEED/CMTA METHOD

Despite the rapid progress in surface crystallography in recent years[1], low-energy electron diffraction (LEED)[2–5] remains the major technique for surface structure determinations.[6] LEED is very well established both experimentally and theoretically.[2–5] However, if LEED structure determinations are to become routine, we need to overcome two theoretical limitations presently suffered by LEED[6]: (i) The time taken to perform a single full dynamic calculation of intensity spectra for a given surface structure scales as the cube of the number of atoms in the surface unit cell, N^3, or at best N^2 (Refs.[2–5]). For a complex surface structure it may take many hours of super computer time.[6] (ii) The conventional trial-and-error method used in LEED makes the time taken to perform a structure search scaling exponentially with the number of structural parameters.[6]

To save the time for performing a single LEED calculation of a model, Lagally *et al.*[7] proposed the constant-momentum-transfer averaging (CMTA) technique in conjunction with kinematic LEED calculations, i.e., the KLEED/CMTA method. It is a very simple method but, unfortunately, just does not work.[8,5] As pointed out by Pendry[8], there are two reasons

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responsible for this. (i) Some influences from the zero-angle scattering (ZAS) remain in the CMTA spectra. (ii) Lack of appropriate effective atomic scattering factors when surfaces consisting of different atoms are studied.

To take advantage of the simplicity of the KLEED/CMTA method meanwhile to overcome the problems of it, we have recently proposed the Quasi-KLEED/CMTA (QKLEED/CMTA) method.[9]

The ZAS influences are threefold[8], i.e., (i) making the CMTA spectra slowly decrease with the electron energy; (ii) modifying the inner potential; and (iii) increasing the peak widths of the CMTA spectra. Pinpointing to these influences, three measures have correspondingly been taken in our LEED intensity calculations[9], i.e., (i) introducing a dumping factor $E^{-\alpha}$ to take care of the first effect; (ii) as first order approximation, treating the inner potential as a constant to be optimized; and (iii) introducing a peak broadening factor, which is to be optimized, to take care of the third effect. Since such calculations have kinematic form but actually they are not real kinematic LEED intensity calculations, thus are, after Pendry[8], called as QKLEED.

In principle, the atomic scattering factors can be treated precisely in QKLEED calculations. However, this means that in order to obtain a theoretical spectrum to be compared with a CMTA spectrum that is the average of, say, 10 I–V curves, one needs to calculate also 10 theoretical I–V curves. To save time, thus to make the structure determinations of complicated surfaces possible, we have introduced the mean complex atomic scattering factor (MCASF) into the QKLEED.[9] With the use of the MCASF, one needs to calculate only one theoretical spectrum to be compared with a CMTA one. Besides, the MCASF itself depends only on the atomic species, diffraction beam, and momentum transfer but not on structural parameters[9], thus needs to be calculated for only once in the course of determining a surface structure. In other words, with the use of the MCASF one can save the time by a factor of about ten.

Although influences of the ZAS could never be eliminated from CMTA spectra, contributions of multiple scattering of other origins can be largely reduced.[7] Clearly, the larger the number of the I–V curves involved in a CMTA spectrum, the wider the area in the $\theta\phi$ (incidence and azimuth angle) space occupied by the incidence geometry, i.e., the (θ, ϕ)'s of the I–V curves, and the more randomly the (θ, ϕ)'s distributing in the $\theta\phi$ space, the better the influence of multiple scattering is eliminated from the CMTA spectra. It has been demonstrated that if the whole $\theta\phi$ space allowed by the conventional LEED optics is utilized and the (θ, ϕ)'s are arranged randomly in it, then less than 10 I–V curves is enough for obtaining a good CMTA spectrum which has the least multiple scattering influence.[9]

These are the major ingredients of the QKLEED/CMTA and their validity has been thoroughly tested with both experiments and full dynamic LEED calculations.[9]

The QKLEED method is so simple that the time taken to perform a single calculation

of the LEED intensity spectra for a given model of a complex surface as Si(111)-(7 × 7) is only a few seconds of personal computer time. However, it is still too slow to perform a complete searching in the whole parameter space of a complex surface structure. Being trapped by local minima is often a serious problem in parameter optimizations if complete search is not carried out. Fortunately, as a result of the simplicity of QKLEED, many optimization procedures[10] could be adopted in it. For example, we have been using the "simulated annealing"[10] in conjunction with other procedures very successfully, and the local minimum problem is practically solved.[9]

II. APPLICATIONS OF QKLEED/CMTA

QKLEED/CMTA has been successfully used to the structure determinations of Cu(001)-(1×1)[9], Si(111)-($\sqrt{3}\times\sqrt{3}$)$R30°$-Al[9], Si(111)-($\sqrt{3}\times\sqrt{3}$)$R30°$-Ag[11], Si(111)-($\sqrt{3}\times\sqrt{3}$)$R30°$-Au, Si(111)-($\sqrt{3}\times\sqrt{3}$)$R30°$-Sn, and Pd(001)-c(2 × 2)-Mn. The major results of the last three surfaces are given here and the details will be published elsewhere.

A. Si(111)-($\sqrt{3}\times\sqrt{3}$)$R30°$-Au

Recently, much attention has been paid to this surface and many plausible models have been proposed for its structure.[12–18] We also studied the surface with QKLEED/CMTA. In our study, we have tested the MTC model[12], honeycomb model[13], trimer model[15], MTLTT model[16], and CHCT model.[17,18] After optimization, the MTLTT model always degenerates towards the CHCT model, while the least total r-factor $R_{vht}^{[19]}$ of the MTC, the honeycomb, and trimer (H_3, T_4, T_1) models was 0.22. In contrast, the total R_{vht} (five integral-order beams and five fractional-order beams) of the optimized CHCT model is 0.159 and its parameters are very close to those determined by recent first principle calculations[17] and full dynamic LEED calculations.[18] Thus we conclude that CHCT is the correct model of the surface. The CHCT model is shown in Fig. 1 and Table 1 shows the comparison of some of its parameters determined by different techniques. The experimental CMTA spectra and their QKLEED counterparts of the model are shown in Fig. 2. A slightly different parameter combination we obtained is also shown in Table 1, which gives a total R_{vht} of 0.162. It is impossible to discriminate either one only based on their R_{vht}. The major difference between the two structures is the distance between the Au atoms and their neighboring Si atoms. In the second structure, this distance is close to the summation of the hard sphere radius of Au and Si, i.e., 1.61 Å. In this regard, this structure is similar to the Si(111)-($\sqrt{3}\times\sqrt{3}$)$R30°$-Ag.[11] To determine which of the two structures is correct further investigations are necessary.

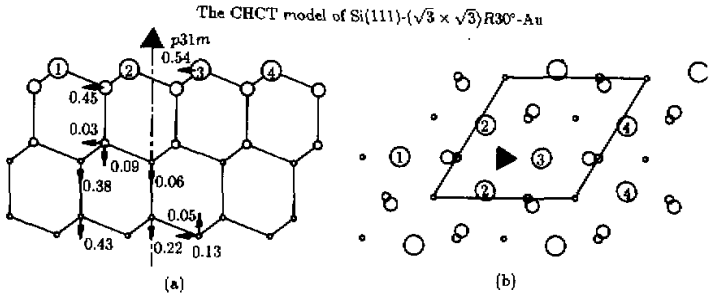

Fig. 1. (a)Side view of the CHCT model with a $p31m$ symmetry, showing all optimized structural parameters of this work. The arrows attached to an atom, which all lie on the figure plane, show the direction of the shifts from its bulk position while the numbers nearby the amount in Å. The shifts of those atoms without arrows can be found according to the $p31m$ symmetry. The vertical distance between the Au layer and the first Si layer is 0.51 Å. (b) Top view of the model with a $\sqrt{3}$ unit cell outlined.

Table 1. Comparison of some of the structural parameters obtained with the first-principle calculations[17], full dynamic LEED calculations[18], and the QKLEED calculations of this work. d: bond length, z: vertical distance, in Å.

	d(Au-Au)	d(Au-Si)	d(Si-Si)	z(Au-Si)
First-principle cal.	2.83	2.45	3.50	0.56
Dynamic LEED	2.80	2.404/2.416	3.50	0.56
QKLEED/CMTA (1)	2.90	2.39	3.51	0.51
QKLEED/CMTA (2)	2.90	2.57/2.55	3.51	1.08

We note that in the full dynamic LEED work[18] the relativistic phase shifts were used. To see if this is indeed necessary, we calculated the MCASF from the relativistic phase shifts and then the corresponding QKLEED spectra. It turned out that the relativistic QKLEED spectra are very close to their QKLEED counterparts (Fig. 3), indicating that the relativistic phase shifts are, at least for this surface, not really necessary.

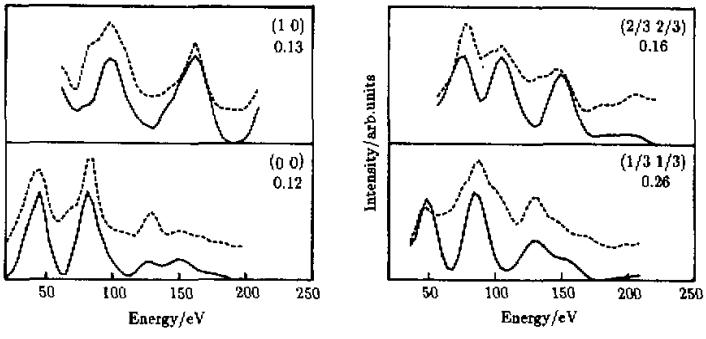

Fig. 2. Comparison of the QKLEED intensity spectra (solid) with their experimental CMTA counterparts (dashed). Shown also in boxes are beam index and R_{vht}. The total R_{vht} of the model's ten beams is 0.159.

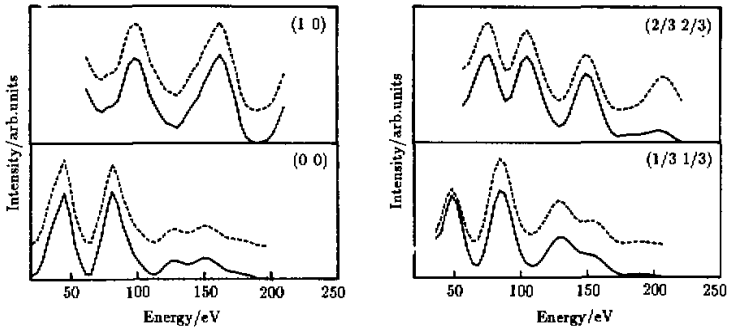

Fig. 3. Comparison of the QKLEED intensity spectra calculated with the use of the relativistic atomic phase shifts of Au (dashed) with those without (solid).

B. Si(111)-($\sqrt{3} \times \sqrt{3}$)$R30°$-Sn

Angle-resolved photoemission study[20] shows that the surface has similar surface states as those of the Si(111)-($\sqrt{3} \times \sqrt{3}$)$R30°$-III surfaces but cannot determine if the adsorption site be T_4 or H_3. Scanning tunneling microscopy[21] and X-ray diffraction[22] studies concluded that the T_4 model is correct. Photoelectron diffraction study cannot discriminate either T_4 or H_3.[23] We have also studied the surface with QKLEED/CMTA. We started from many very different structures of both the H_3 and T_4 model. For the H_3 model, optimization always resulted in the almost same structure, with the maximum parameter difference being only 0.03 Å. The total R_{vht} of its ten beams was 0.16, its bond lengths being within 6% of the bulk value. For the T_4 model, however, even if we do not care about the bond lengths the least R_{vht} was 0.18. What is even worse is that the agreement of its fractional-order beams was worse. Thus we reach the conclusion that H_3 is the real adsorption site of Sn on the surface.

C. Pd(001)-c(2 × 2)-Mn

To see if the method works for alloys, we studied the Pd(001)-c(2 × 2)-Mn surface. The optimized structure of our study was very similar to what was determined by full-dynamic LEED calculations.[24]

III. SUMMARY

To make LEED a routine technique for surface structure determinations, we have, pinpointing to the problems of the conventional KLEED/CMTA, proposed a new QKLEED/CMTA method. In this method the effects of the zero-angle scattering are taken into account in such a way that they have essentially no influence on reaching the correct structural parameters. Meanwhile, a mean complex atomic scattering factor is introduced to it so that it is applicable to surfaces consisting of different atoms. The simplicity of the

method allows many powerful schemes of optimization to be adopted.

The QKLEED/CMTA method has been carefully tested with experiments and full dynamic LEED calculations from every possible direction we could think of, while its capability of reaching the right structural parameters has been demonstrated on many different surfaces, such as the $\sqrt{3}$ structures of Al, Ag, Au, and Sn on Si(111) substrate.

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