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THE SIMULATED ANNEALING GLOBAL SEARCH ALGORITHM APPLIED TO THE CRYSTALLOGRAPHY OF SURFACES BY LEED

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Surface structure determination by Low Energy Electron Diffraction (LEED) is based on a comparison between experimentally measured and theoretically calculated intensity versus energy $I(V)$ curves for the diffracted beams. The level of agreement between these, for different structural models, is quantified using a correlation function, the so-called R factor. Minimizing this factor allows one to choose the best structure for which the theoretical simulations are computed. Surface structure determination thus requires an exhaustive search of structural parameter space in order to minimize the R factor. This minimization is usually performed by the use of directed search methods, although they have serious limitations, most notably their inability to distinguish between false and real structures corresponding to local and global R factor minima. In this work we present the implementation of a global search method based on the simulated annealing algorithm, as suggested earlier by Rous, using the Van Hove and Tong standard LEED code and the results of its application to the determination of the structure of the Ag(111) and CdTe(110) surfaces. Two different R factors, R_P and R_1, have been employed in the structural searches, and the statistical topographies of these two factors were studied. We have also implemented a variation of the simulated annealing algorithm (Fast Simulated Annealing) and applied it to these same two systems. Some preliminary results obtained with this algorithm were used to compare its performance with the original algorithm proposed by Rous.

1. Introduction

Surface structure determination by LEED is based on a comparison between experimental and theoretical intensity versus energy $[I(V)]$ curves of the diffracted beams. This comparison is aided by the use of a so-called reliability factor, or R factor, that quantifies the agreement between experimental

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and theoretical $I(V)$ curves.[1] By minimizing this R factor it is possible to determine the best-fit structure among all the structural models considered. Surface structure determination by LEED is therefore effectively a search problem in which one seeks to locate the global minimum of the R factor in the multidimensional parameter space formed by the structural and nonstructural variables.

Until recently, the majority of the LEED structure determinations have been performed by employing an exhaustive trial-and-error exploration of this parameter space. In this method, all physically feasible combinations of structural parameters are investigated, usually by calculating the R factor characterizing the level of agreement between calculated and theoretical $I(V)$ curves on a grid that extends over a representative part of the parameter space. This exhaustive search demands a lot of computing time, and the effort scales exponentially with the number of varied parameters. As Pendry[2] has indicated, the exhaustive LEED search belongs to the class of the NP-complete optimization problems, which requires a computational effort to locate the solution that is not bounded by a polynomial in N. Such a class of problems is of special importance in the theory of numerical analysis, since even greater improvements in the speed of computer hardware cannot make a significant impact on the size of the NP-complete problem.

More recently, local directed-search methods have been applied to surface structure determination. These methods are based upon descent methods, converting the N-dimensional search into a sequence of N one-dimensional searches. The exploration of the local topography of the R factor hypersurface improves the efficiency of the structural search. The first gradient method, using fully dynamical calculations, was developed by Cowell and de Carvalho.[3] Lately several descent methods have been employed by the Berkeley group, always using the efficient Tensor-LEED approach,[4] while the Munich group has implemented a gradient expansion method that goes beyond a simple descent method.[5,6] Descent methods, compared to the exhaustive search approach, can offer substantial improvements in the scaling of the search effort, since the scaling relation presented by the gradient methods in actual LEED searches is approximately N^2.

The major problem associated with directed-search methods is that they can locate only one R factor minimum, and are unable to distinguish between local and global minima. A typical procedure employed to locate the global minimum using directed-search methods is to launch several searches from different initial structures.[4] With this scheme one hopes to locate all R factor minima, including the global minimum. However, since the number of initial structures scales exponentially with the number of parameters to be varied, this scheme is also an NP-complete problem. Moreover, there is no certainty that all local minima can be located, particularly with a complex (nonuniform) distribution of local R factor minima. Despite these problems, descent methods have been used successfully in surface structure determination by LEED.[7–9]

In view of the problems associated with local search methods, there is clearly interest in the possibility of applying global search algorithms to studies of surface crystallography by LEED. A global search algorithm for this purpose must be able to identify the global R factor minimum amongst all the local minima and to present a reasonable scaling relation when compared to the exhaustive search or to multiply launched local searches (descent methods). A global search method which offers these features is the "Simulated Annealing Algorithm" (SA), which has attracted significant attention, having been applied successfully to solve large-scale optimization problems in physics, chemistry, statistics, neural networks, engineering and economics.[10] In a recent paper Rous[11] has proposed utilizing the simulated annealing algorithm to R factor minimization in LEED analysis. The algorithm was applied to a search for the global R factor (Pendry R factor[12]) minimum of the hypersurface generated by a theory–theory comparison of $I(V)$ curves calculated for the Ir(110)(1×2) surface. Its performance was evaluated, and a scaling relation with respect to the number of varied parameters was obtained. A simple statistical analysis of the topography of the R_P hypersurface was used to improve the efficiency of the method, enabling faster convergence of the search.

More recently two other papers related to this subject have been published. Döll and Van Hove[13] have proposed the application of the genetic algorithm, which simulates the natural evolution of living organisms, to the LEED structural search problem.

They also applied the genetic algorithm to a theory–theory comparison in the Ir(110)(1 × 2) system and evaluated its performance. Although a scaling relation was not presented, the results obtained with the optimization of three structural parameters indicate that the genetic algorithm was able to find the final structure about 10 times faster than an exhaustive grid search. This factor is likely to increase significantly if more structural parameters are investigated.

Another approach to the global optimization problem was suggested by Kottcke and Heinz.[14] A modified random sampling algorithm which only allows downhill steps (in contrast to simulated annealing) was proposed. It performs a global search as long as the R factor values are high, and becomes increasingly local when the agreement between theory and experiment improves. This algorithm was again applied to theory–theory comparison in the Ir(110)(1 × 2) system, but also to real experimental data from two different surface phases of FeAl(100) and to data from $Mo_{0.95}Re_{0.05}$(100)-c(2 × 2)-C. The results obtained for the Ir(110)-(1 × 2) system indicate a scaling relation given by $N^{2.5}$.

In the present work we have applied the simulated annealing global search algorithm (SA), as proposed by Rous,[11] to the structure determination of the Ag(111) and CdTe(110) surfaces, using sets of experimental $I(V)$ curves collected for both systems. The topographies of the corresponding R_P and R_1 (linear X-ray factor)[1,15] hypersurfaces for the Ag(111) system, and of the R_P hypersurface for the CdTe(110) surface, were studied. We have also investigated the performance of a variation of the simulated annealing algorithm, "Fast Simulated Annealing,"[16] to surface structural searches for the same two systems.

2. The Simulated Annealing Algorithm

The simulated annealing algorithm[17–19] as discussed above is a technique that has attracted a lot of attention, as it is suitable for optimization problems of large scale, especially ones in which the desired global minimum is located among many shallower local minima. The wide range of possible applications of this method, always associated with problems that require the minimization of a "cost function," can be explained by two of its main features: that it can be applied when little or no detailed information is available concerning the specific nature of the optimization problem, and that it is easily incorporated into any kind of source code.

The main feature of the simulated annealing algorithm is that it is a probabilistic hill-climbing algorithm, i.e. during the search process the moves that increase the cost function (uphill moves) are accepted in addition to moves which decrease the cost function. This is the central point that enables the search algorithm to locate the global minimum among all the other local minima. At the heart of the simulated annealing algorithm is the Metropolis criterion[20] which controls the acceptance probability of every step of the search. Starting from an initial point A, a random step δX is chosen, leading to a new point B. The change of the cost function $\Delta C = C(B) - C(A)$ is evaluated. If the cost function change is negative ($\Delta C \leq 0$) the move will be accepted (a downhill move); if $\Delta C > 0$ the uphill move will be accepted with a probability given by the Boltzmann distribution $P(\Delta C) = e^{\frac{-\Delta C}{T}}$. This probability is controlled by the dimensionless parameter T (an artificial temperature), which is gradually decreased during the search. The simulated annealing algorithm is basically a search based on randomly choosen steps, accepted or rejected according to the Metropolis criterion, together with a gradual reduction of the "temperature" T.

The main challenge in improving the performance of the simulated annealing method is to lower the "temperature" the fast as possible, but to ensure that one does not get trapped in a local minimum. The objective is thus to find the quickest annealing that achieves a value for the probability of finding the global minimum equal to, or near to, unity. An interesting step taken along this search was the work of Szu and Hartley,[16] who proposed the use of a Cauchy–Lorentz visiting distribution, instead of a Gaussian or uniform distribution as is commonly used, for the choice of the random moves. In this case the search distribution is semilocal, i.e. the random moves are frequently local, but occasionally long moves can also be considered. With this scheme, called *Fast Simulated Annealing* (FSA), the cooling cycle can be much faster when compared to the other implementations, making the search quite more efficient. In order to illustrate the visiting probability of the FSA and of the commonly employed implementations of the simulated annealing (Gaussian and uniform distributions), one can use a one-dimensional

double-well cost function, as presented in Fig. 1. The Cauchy–Lorentz and the Gaussian distributions (which are "temperature"-dependent) and the uniform distribution ("temperature"-independent) are also plotted over the shallower minimum (Fig. 1 — point A), representing a "trapping" in the local minimum. We can see that while the "wing" of the Cauchy/Lorentzian distribution has reached the deeper minimum (Fig. 1 — point B), the normal (Gaussian) distribution has a negligible value at the deeper minimum and thus offers much less chance to escape from the initial local minimum. The uniform distribution will only be capable of escaping from the local minima after a lot of favorable steps, also therefore presenting a lower probability. In the Cauchy–Lorentz scheme, a higher "temperature" implies a faster sampling in a much more coarse-grained fashion. As the "temperature" is gradually reduced the search becomes more refined in its sampling.

In recent work Rous[11] has implemented the simulated annealing algorithm using the Van Hove–Tong conventional LEED[21] code and discussed its performance by applying it to a simple structural search. The method was applied to locate the global minimum of the Pendry R factor (R_P) hypersurface generated by a theory–theory comparison of $I(V)$ curves calculated for the Ir(110)(1 × 2) system. A scaling relation for the number of selected structures before convergence in the search as a function of the number of varied structural parameters was obtained. Additionally, a statistical analysis of the topography of R_P was performed, allowing a better definition of the control parameters of the cooling scheme and, as a consequence, a faster convergence of the search ("quenching transition"[11]). In the Rous implementation of simulated annealing the random steps were chosen according to a uniform distribution, their size being constrained to a maximum value that was not "temperature"-dependent.

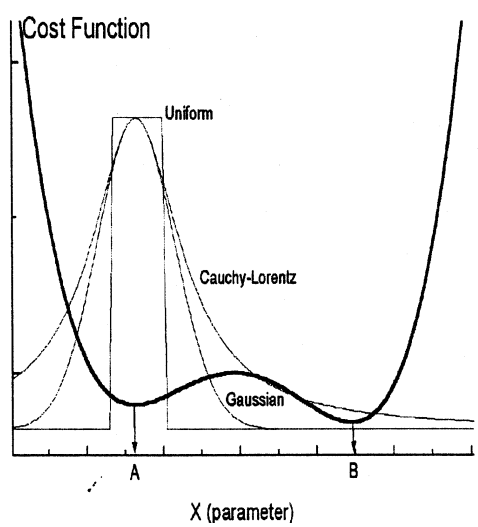

Fig. 1. Comparison between the Cauchy–Lorentz, Gaussian and uniform distribution sampling. The Cauchy–Lorentz and Gaussian distributions are plotted at the same "temperature."

The goal of the present work is to apply the simulated annealing algorithm to actual surface structure determinations of the Ag(111) and CdTe(110) systems. We have implemented the simulated annealing method using the Van Hove and Tong conventional LEED code, using the scheme proposed by Rous, but also implementing the "Fast Simulated Annealing,"[16] in order to explore its performance as compared to the conventional SA approach. We have chosen the Ag(111) and CdTe(110) systems because both of them were recently the subject of quantitative structure determinations carried out at our laboratory, where the LEEDFIT code was used.[7,22–27] The two systems are also suitable for testing the performance of the SA algorithm, the number of structural parameters involved being significantly larger for the CdTe(110) surface structure determination than in the case of the Ag(111) surface.

3. Experimental Details

The Ag(111) data set was collected at the University of Warwick using a UHV chamber equipped with a range of facilities for sample preparation and surface characterization. This system was also provided with a TV camera system combined with a rear-view LEED optics and the base pressure of the chamber was typically $1-2\times10^{-10}$ Torr. The Ag(111) surface sample was obtained from an Ag single crystal oriented by Laue X-ray diffraction and cut using spark erosion. The surface was then polished using progressively finer grades of diamond paste to produce a mirror finish. After insertion in the vacuum chamber, the sample was cleaned using cycles of ion bombardment (Ar^+ ions with 3 keV) and annealing (500°C for 10 min). The temperature was monitored using a chromel–alumel thermocouple in contact with the sample. The cleaning cycles were repeated until no carbon, oxygen or sulphur were detectable using

XPS, while LEED indicated a sharp (1×1) pattern. The temperature of the Ag(111) sample was then decreased to $-110°$C using a liquid nitrogen cooling system and the diffracted beam intensities of the LEED patterns from 70 eV to 400 eV were digitized using an Omicron LEED Star video system at nominal normal incidence. The $I(V)$ curves of a total of 16 diffracted beams were obtained, normalized with respect to the incident beam current, and smoothed using a five-point least-square cubic polynomial algorithm.

The CdTe(110) experimental data set used in this work was collected using a UHV chamber equipped with a range of facilities for sample preparation and surface characterization together with a computer-controlled LEED diffractometer at the Physics Department of UFMG, Brazil. The base pressure of the chamber was typically 5×10^{-10} Torr. The CdTe crystal was cleaved in air and the exposed (110) surface showed a planar and mirror finish. After insertion in vacuum, the sample was cleaned using 500 eV Ar^+ ion bombardment for 10 min. After this, the surface exhibited a sharp (1×1) pattern and no carbon, oxygen or sulphur were detectable using Auger Electron Spectroscopy. The LEED patterns for the CdTe(110) surface were then recorded from 20 up to 150 eV using an Omicron video-LEED system in a scattering geometry near normal incidence. The sample was mounted on the manipulator in such a way that the parallel component of the incident wave vector laid on the mirror plane of the surface. With this setup, the symmetry between symmetric beams was preserved and the value of the azimuthal angle ϕ was constrained to one of the following two values: $0°$ or $180°$. The $I(V)$ curves for 10 diffracted beams were then obtained from the digitized LEED patterns, normalized with respect to the incident beam current and smoothed using a five-point least-square cubic polynomial algorithm. Again, each of these 10 $I(V)$ curves was used as a separate data set in the R factor calculation for the structure determination.

4. Computational Details

The implementation of the simulated annealing algorithm using the Van Hove–Tong conventional LEED

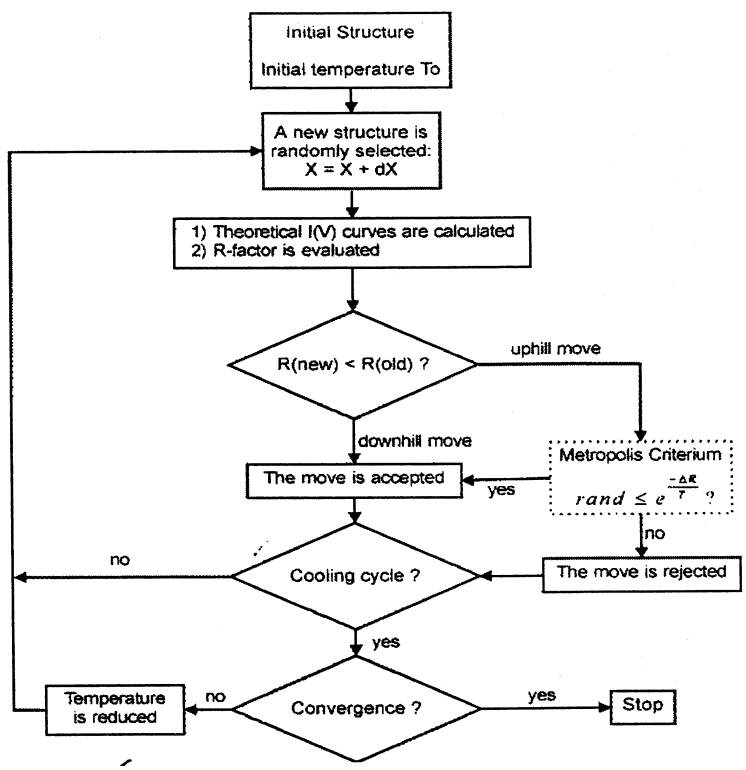

Fig. 2. Flow chart of the simulated annealing algorithm implementation for the LEED structure search.[11]

source code was performed according to the scheme proposed by Rous.[11] A flow chart of this implementation is presented in Fig. 2.

In order to test out the simulated annealing algorithm it was first applied to the Ni(100) system, exploring the R_P hypersurface generated by a theory–theory comparison. The distance between the first and second layers was varied within a limit of 0.4 Å, centered at the bulk-terminated value. The SA algorithm has shown to be able to locate the global minimum between a lot of other poorer local minima in this one-dimensional structural search. Then, the program was adapted in order to be used for the Ag(111) and CdTe(110) surfaces.

The theoretical analysis was performed assuming a muffin-tin model of the potential for both Ag(111) and CdTe(110). Muffin-tin radii of 1.45 Å for the Ag atoms and 1.40 Å for the Cd and Te atoms were used. Atomic wave functions were used to calculate the scattering potential and a Slater parameter $\alpha = 2/3$ was assumed in the local exchange approximation. The phase shifts were evaluated by the integration of the radial part of the Schrödinger equation in the muffin-tin spheres. Theoretical $I(V)$ curves were calculated using the Van Hove–Tong conventional LEED code in the Reverse Forward Scattering approximation. The calculations were performed on personal computers (Pentium MMX 200 MHz and AMD K6-300 MHz) running the Linux operating system for Ag(111) and on an Alpha-Dec station for CdTe(110). Eight phase shifts were employed in the calculations and inner potentials of $V_0 = (-10 + 4i)$ eV for Ag(111) and $V_0 = (-1 + 5i)$ for the CdTe were assumed; their real parts were optimized during each analysis.

5. Results and Discussion

In the Ag(111) structural search the layer spacings between the first and second layers and between the second and third layers were allowed to vary in a parameter space volume of 0.4×0.4 Å^2 using the bulk-terminated surface structure as a reference. The SA algorithm was run to search for R_P and R_1 global minima launched from many different starting structures. The general scheme used in these searches was

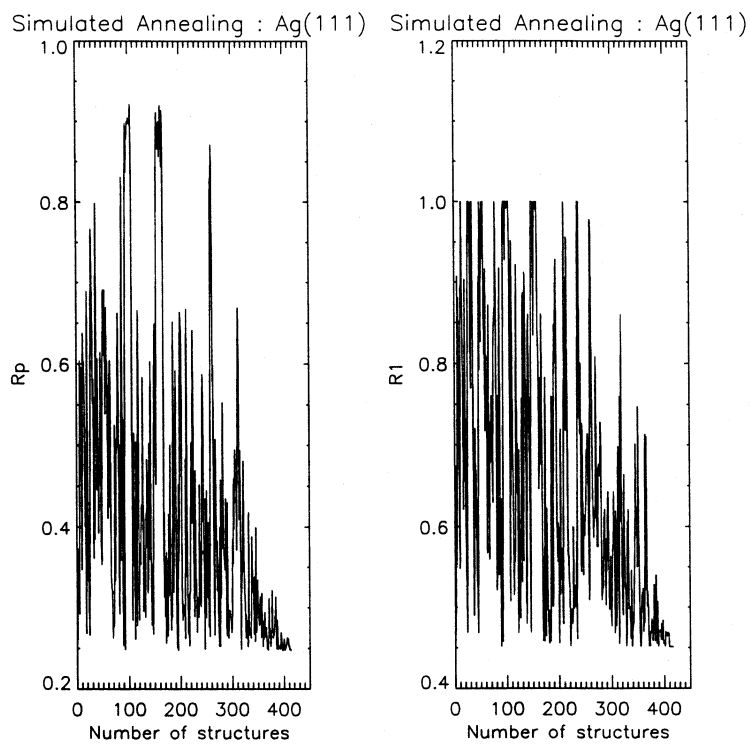

Fig. 3. R_P and R_1 for Ag(111) plotted as a function of the number of trial structures investigated during the search using the SA algorithm.

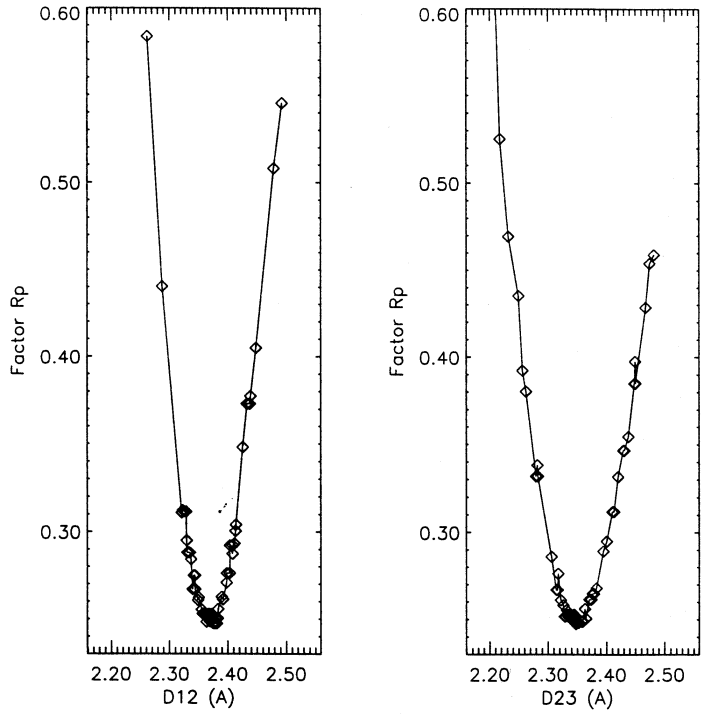

Fig. 4. R_P as a function of d_{12} for $d_{23} = 2.34$ Å and as a function of d_{23} for $d_{12} = 2.37$ Å. These fixed values of the interlayer spacings correspond to the best-fit structure.

the one proposed by Rous,[11] i.e.:

- Random steps: chosen from a uniform distribution, within the range $0 \leq |\delta X| \leq 0.1$ Å.
- Cooling cycle: starting from an initial "temperature" of 0.8; every 30 structures the "temperature" was decreased following the rule $T_{n+1} = \alpha\, T_n$, with α=0.85.

Figure 3 shows plots of the R factors as a function of the number of structures investigated for typical searches.

For all the searches carried out for both R factors, the SA algorithm always converged to an expected "bulk-terminated" surface structure, after about the same number of trial structures. The errors in the layer spacings d_{12} and d_{23} were obtained from the dependence of the R factor on these parameters around the minima as shown in Fig. 4.

As may be seen from the contour plots of the R_P and R_1 hypersurfaces, (shown in Figs. 5 and 6, respectively), there is a single minimum at the expected bulk-terminated surface within the volume of parameter space explored.

The final structure obtained is in agreement with a recent LEED structural study performed using the LEEDFIT code[22–26] for Ag(111) data collected at room temperature.[27]

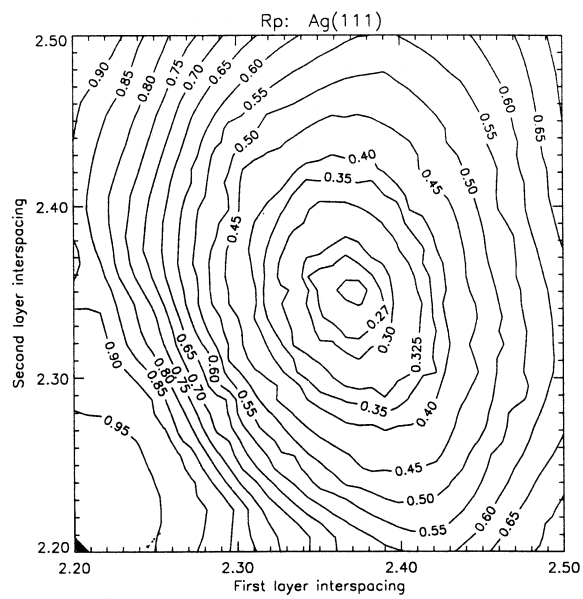

Fig. 5. R_P contour plot of the explored parameter space (0.4×0.4) Å^2. This contour plot was generated by a number of points (explored structures) of the order of 10^3.

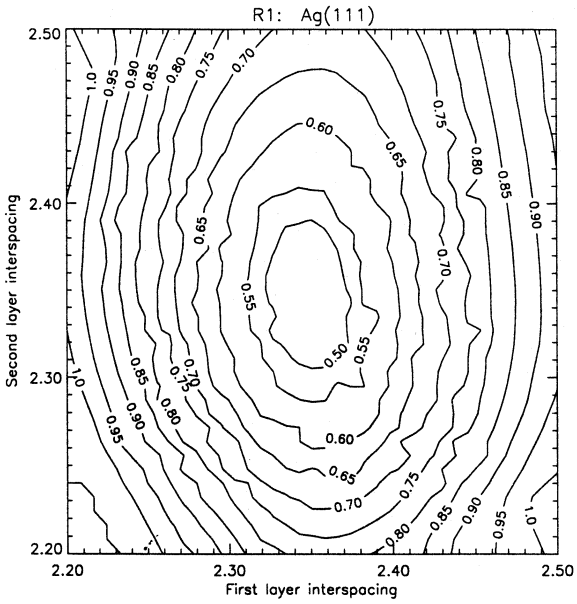

Fig. 6. R_1 contour plot of the explored parameter space (0.4×0.4) Å^2. This contour plot was generated by a number of points (explored structures) of the order of 10^3.

As previously discussed, the great challenge in the improvement of the simulated annealing algorithm is to decrease the "temperature" as fast as possible, but ensuring that the search will not get trapped in a local minimum. Hzu and Hartley[16] have proposed a modified version of the SA algorithm, the "Fast Simulated Algorithm" (FSA), which allows faster cooling when compared with the traditional implementations. Following their ideas we modified the SA algorithm, according to the following scheme:

- Random steps: chosen according to a Cauchy–Lorentz distribution $G(\delta X) \approx T_n/(T_n^2 + \delta X^2)$, allowing occasional long steps. [$T(n)$ corresponds to the "temperature" in the cooling cycle n.]
- Cooling scheme: a faster cooling scheme was adopted — at every new structure the "temperature" was decreased according to $T_n = T_0/n$.

This new algorithm (FSA) was used for the Ag(111) system, following the same strategy used with the SA algorithm, namely that the first two interlayer spacings were varied within the parameter space volume of 0.4×0.4 Å^2 referenced to the bulk-terminated structure. The searches were launched

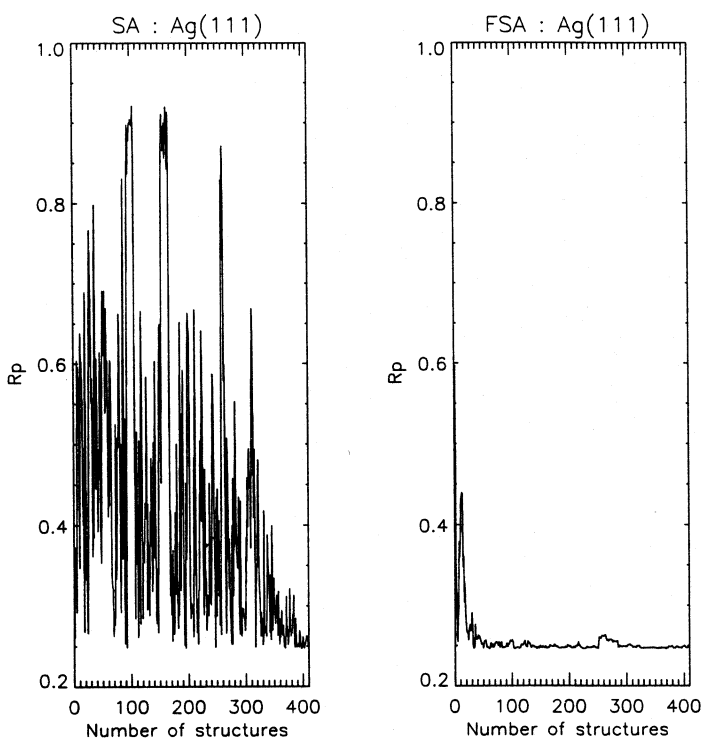

Fig. 7. Comparison between the typical results of the structural search for the Ag(111) system employing the conventional and the fast simulated annealing. Both searches were launched from the same initial structure.

from different initial structures and, in all cases, located the global minimum. However, much faster convergence was achieved that with the conventional SA algorithm. As can be seen in Fig. 7, convergence occurred after about 100 tested structures. This is a very encouraging result.

However, the R_P hypersurface topography within the parameter space investigated for the Ag(111) system is quite simple, showing only a single minimum, so the ability of the algorithm to escape from a local minimum has not been proved. In order to investigate this point, the program was launched from a point located in a secondary minimum that corresponds to a diffraction coincidence. The diffraction coincidences occur because the Bragg condition is satisfied in a periodic fashion as an atom is displaced through half of the electron wavelength ($\langle \mathbf{k} \rangle . \delta \mathbf{r} \approx 2\pi$).[1,21] The parameter space volume investigated was of 1.0×1.0 Å^2, again using the bulk-terminated structure as a reference. A slower cooling scheme was then used. Starting from an initial "temperature" of 0.8 (see Sec. 2), at every five new structures the "temperature" was decreased according to $T_n = T_0/n$. As may be seen from Fig. 8, to locate the global minimum (Fig. 8 — point B — $R_P = 0.23$), the FSA search needs to escape from the local minimum (Fig. 8 — point A — $R_P = 0.55$) and to perform many uphill moves.

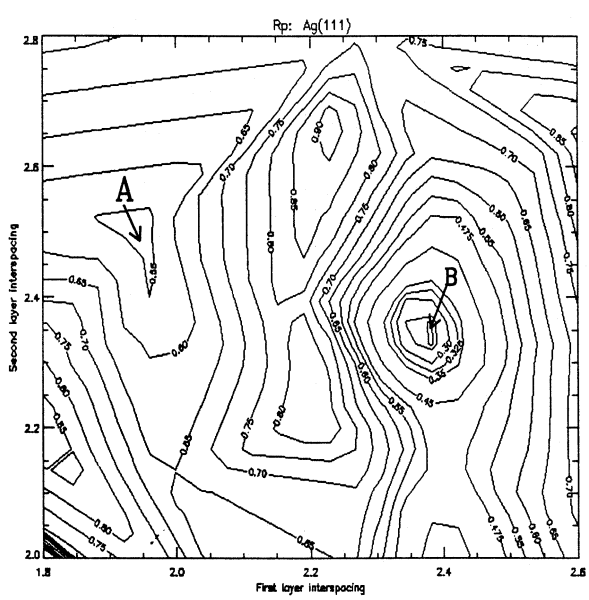

Fig. 8. Contour plot of the R_P hypersurface. Point A corresponds to a local minimum (coincidence minimum) and point B to the global minimum.

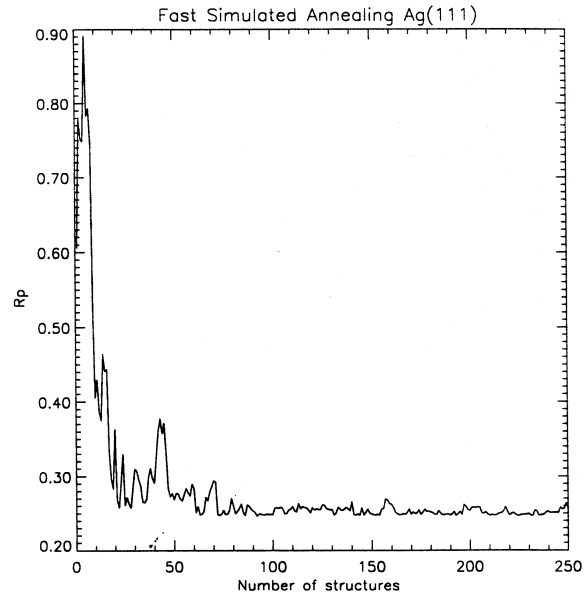

Fig. 9. R_P as a function of the number of trial structures for the Ag(111). The search was launched from a secondary minimum corresponding to a diffraction coincidence.

In spite of the complexity of this R_P hypersurface, the FSA was able to reach the global minimum after typically 10^2 trial structures (Fig. 9). Based on these results, we may conclude that the FSA approach does seem to be useful in LEED surface structure determination for simple systems such as Ag(111).

The main remaining question concerns how well this algorithm works under more complex situations, especially when a large number of parameters have to be investigated. In order to cast some light on this problem we have run the FSA program for the CdTe(110) surface. This surface, as indicated by previous work,[3,7] presents a complex reconstruction. The top layer is characterized by a bond-length-conserving rotation and a contraction towards the substrate. Because of the complexity of this reconstruction, its structure determination is quite complicated, with a large number of structural parameters to be optimized: eight parameters if the positions of atoms in the first two layers are allowed to vary, or four parameters if only the outermost layer atom positions are varied. The CdTe(110) surface is therefore an interesting system to be analyzed using the simulated annealing algorithm.

In order to compare the performance of the SA and FSA algorithms for this more complex

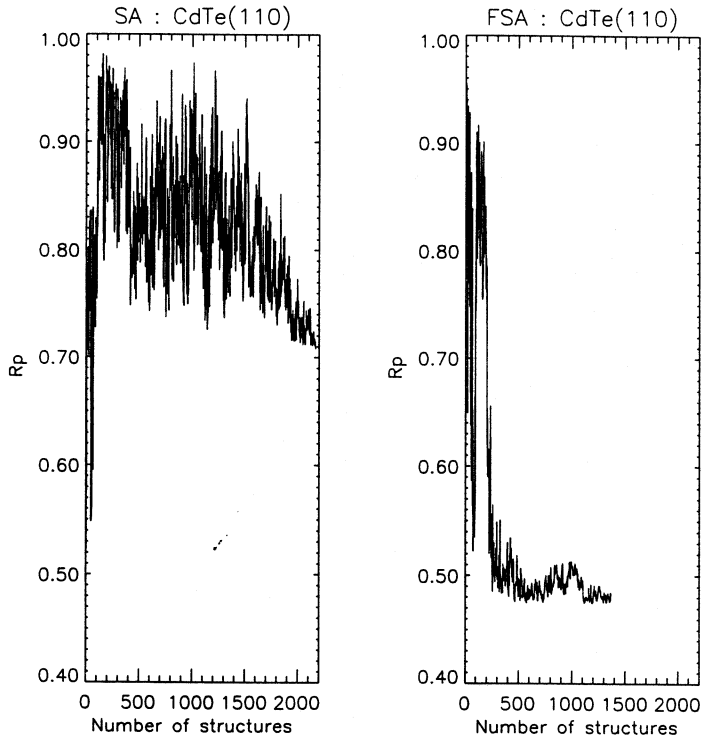

Fig. 10. Comparison between typical results obtained with the SA and FSA structural searches employed for the CdTe(110) system.

structure determination, the program was run from different starting structures. As the main point to be investigated here was the performance of the two algorithms, our first attempt was to allow the four parameters associated to the first layer atoms to vary, and the second layer atoms were kept in their bulk positions. A parameter space hypervolume of $(1.0 \times 1.0 \times 2.0 \times 2.0)$ Å^4 was searched. The cooling schemes used in the SA searches was identical to that used for the Ag(111) system, with an initial "temperature" of 0.8. For the FSA searches the same initial "temperature" was used but a slower cooling scheme was employed: at every 10 new structures the "temperature" was decreased according to $T_n = T_0/n$. Some preliminary results can be seen in Fig. 10. The SA searches at this cooling rate were not able to locate the minimum, even after typically 2000 trial structures. By contrast, the FSA algorithm always located the minimum after about 1000 trial structures. Although these preliminary results come from a search where only a few parameters were varied, and therefore the fit cannot be regarded as the global minimum, the improvement in the time of convergence to locate the minimum using the FSA, compared to the SA, is indeed very encouraging.

The results we have obtained so far are not enough to obtain the scaling behavior for the FSA, but it is clear that for the Ag(111) system where two parameters were varied the FSA is about eight times faster than the SA. For the CdTe(110) system we do not have the correct scaling but it can be seen that the FSA is at least twice as fast as the SA. At this point in the work we are not able to compare the effectiveness of the FSA algorithm with that of other global search methods proposed by Döll and Van Hove[13] and by Kottcke and Heinz.[14] However, calculations including a greater number of parameters for the two systems are underway in order to understand the scaling behavior of the algorithm. The influence of the cooling rate of the search process on the probability of finding the global minimum, which must not be distinguishable from 1, is also under investigation.

6. Conclusions

In this work we have investigated the application of the simulated annealing (SA) global search algorithm to the determination of the structure of surfaces by LEED. The algorithm was implemented with the

Table 1. Vertical spacings for the best R_P and R_1 structural models. d_{12} and d_{23} correspond to the distances between the first and second and between the second and third layers respectively.

Vertical spacing	R_P model	R_1 model	"Bulk-terminated" model
d_{12}	(2.37 ± 0.02) Å	(2.35 ± 0.02) Å	2.3589 Å
d_{23}	(2.34 ± 0.03) Å	(2.35 ± 0.04) Å	2.3589 Å

Van Hove–Tong conventional LEED code using the scheme suggested by Rous.[11] Structural searches using the SA algorithm have been performed for the Ag(111) system, using the R_P and R_1 factors, and the final structures obtained indicate that the surface is ideally bulk-terminated (Table 1).

A variation of the SA algorithm, the Fast Simulated Annealing (FSA),[16] was also implemented and applied to the structure determination of the Ag(111) surface. A comparison of the results obtained with the two algorithms showed that the FSA converges faster and, even with a faster cooling scheme, it was able to locate the global minimum of the R_P hypersurface, without getting trapped into a local minima.

For the CdTe(110) system, preliminary results show that only the FSA algorithm seems to be able to locate the global minimum, under the cooling schemes performed for the SA and FSA searches.

Although more detailed studies are necessary, the FSA algorithm appears as a very efficient search scheme, allowing faster convergence and a lower probability of getting trapped in local minima. It may therefore be a promising alternative search method for structure determination by LEED.

Acknowledgments

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