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EXPERIMENT AND THEORY

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Low-Energy Electron Diffraction - Experiment and Theory

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Summary

The current state of structure determination using Low-Energy Electron Diffraction (LEED) intensities is reviewed. Experimental and theoretical advances are examined, while lessons from successes and failures are discussed. The relationship between LEED and other techniques is also covered.

1. Introduction

LEED has developed considerably in the last decade [1-3]. Indeed, structure determination by LEED has been applied to an ever increasing diversity of surfaces. At the same time, the underlying theory and calculational methods have also been diversified to treat new types of structures, while the experimental accuracy, speed and reliability have improved.

Figure 1 presents a year-by-year and a cumulative count of surface structure determinations by LEED. All other techniques combined have not yielded this many detailed surface structures. On the other hand, LEED often needs input from other techniques to guide its structural search.

The following discussion reviews these and other issues in the present state of surface crystallography by LEED.

2. Experimental Developments

The main experimental innovation in LEED intensity measurements is the widespread introduction of automated video-LEED systems [4]. These allow a rapid extraction of the raw intensity data from the UHV chamber, followed by a rapid conversion to normalized and background-corrected beam intensities. The time required to produce a full set of I-V (i.e. intensity-voltage) curves has thereby been reduced from many hours to minutes. This time reduction alone enhances the reliability of the data by enabling errors and inaccuracies to be more readily detected and corrected. The time reduction also limits the damage

induced by the electron beam, especially for sensitive overlayers.

A further innovation, not yet wide-spread, is "digital LEED" [5,6]: here the traditional screen is replaced by a position-sensitive detector coupled to electronic counters. The main benefits are the lack of conversions from electron current to optical intensity and back again, and the much reduced incident beam current ($\sim 10^{-6}$ times that of conventional systems). It will also simplify the measurement of diffuse LEED intensities, which will be important in connection with the introduction of structural determination of disordered surfaces (see next section).

3. Theoretical Developments

The basic ingredients of LEED theory have not changed in the last decade, because they have proved adequate [1-3]. For instance, the muffin-tin model with a constant imaginary part of the potential and the Debye-Waller factor remain in effect. It has repeatedly been found that correct structural parameters are the more important input to a LEED calculation. In other words, LEED is more sensitive to atomic coordinates than to non-structural parameters (at least at kinetic energies above about 30 eV).

The recent theoretical developments have focussed on improving the treatment of multiple scattering, in order to reduce the computational costs. This is essential because increasingly complex surface structures are being investigated and the conventional cost rises with a high power of the complexity.

The theoretical methods of the early 1970's were designed for the worst-case

situation of strong multiple scattering in compact metal surfaces. But many structures of interest (semiconductor surfaces and most non-metallic overlayers) involve less extreme multiple scattering. Thus, new methods have been introduced to take advantage of this fact. An example is the Beam Set Neglect method [7] designed for overlayers which have large unit cells. With this method, the cost of a structure determination can be made similar to that of a $c(2 \times 2)$ or (2×1) overlayer calculation, whatever the size of the unit cell. For instance, in a recent structural determination of a coadsorbed overlayer of benzene and carbon monoxide, each of about 1000 structures tested cost approximately US\$3 [8]. Other effective methods for reducing the computational costs are the "cluster" approach [9] and the "near-neighbor multiple scattering" [10] approach.

A new direction for LEED crystallography is its application to disordered surfaces, especially disordered overlayers. This direction differs from the more established and continually flourishing study of two-dimensional order, disorder, phase transitions, and defects using the LEED pattern [11]. There is considerable evidence that the diffuse LEED intensity contains, besides two-dimensional ordering information, the same kind of three-dimensional structural information as do the sharp beams due to ordered surfaces: layer spacings, bond lengths, bond angles. Thus, "diffuse LEED" could compete with Angle-Resolved Photoemission Extended Fine Structure (ARPEFS), Surface Extended X-ray Absorption Fine Structure (SEXAFS), Near-Edge X-ray Absorption Fine Structure (NEXAFS), etc., in studying the short-range structure of disordered overlayers, without incident x-rays. The LEED theory has recently been developed for this application [12] and awaits comparison with experimental data.

4. Successes and Failures of LEED Crystallography

Among the successes of LEED one should mention the diversity of surfaces to which it has been applied: from clean, reconstructed metal and semiconductor surfaces to large adsorbed organic molecules, via ionic insulating materials, layer materials and alloys; to name some major categories. Few techniques possess this range of applicability.

An instructive example of success concerns the discovery of multilayer relaxation at non-compact metal surfaces, such as Al(110) [13], Cu(110) [14] and Fe(310) [15]. Here the interlayer spacing (perpendicular to the surface) varies from one layer to the next down to a depth of about four layers below the surface, where it settles to the constant bulk value. This case illustrates the growing evidence that the failure to solve a structure usually is due to failure to try the correct structure. The most recent example of this is the reconstruction of Au(110) with a (1x2) unit cell. The "missing-row" model has for some time been favored by LEED, most clearly for the related reconstruction of Ir(110)-(1x2), but the structure could not be called settled at all. However, a new LEED analysis allowing for deeper-layer relaxations in Au(110)-(1x2) gives quite good results: consequently, the missing-row model with a second-layer row-pairing, a third-layer buckling and suitable top, second and third interlayer spacings can be accepted now as the structural solution [16].

Other notable successes include the following. For the system Ag(100)-c(2x2)-Cl, band structure calculations compared to photoemission data at first disagreed with LEED structural results. Agreement with LEED was subsequently obtained with new photoemission calculations and new photoemission data. It

appears that the initial photoemission data base was too small for proper structural determination, while the usually large LEED data base provided a more reliable determination [17].

Regarding molecular adsorbates, half a dozen structures of carbon monoxide associatively adsorbed on several metal surfaces have been solved by LEED [18]. They all produce metal-carbon and carbon-oxygen bond lengths in good agreement with corresponding bond lengths known in metal carbonyl clusters (within $\sim 0.05\text{\AA}$). In addition, the CO binding site determination (top, bridge or hollow) matches perfectly the assignment based on C-O stretch frequencies, including the recent case of CO in a hollow site on Rh(111), due to coadsorbed benzene [8].

There are several problematic determinations to be commented upon here. While atomic adsorbates on metal surfaces have generally yielded very good results, the case of oxygen adsorption is rather unsatisfactory. This applies to oxygen on Ni(100), Ni(110), Cu(110), Al(111) and other surfaces. Based upon the above-mentioned successes of LEED crystallography, it is plausible that these failures are due to an incomplete structural search. The small oxygen atoms can indeed readily penetrate between metal atoms and even reconstruct the metal surface. This opens up many structural possibilities, many of which have not been tried in LEED calculations. The same difficulty is illustrated by the Si(100)-(2x1) [19] and Si(111)-(2x1) structures [20]: after many years of structural searching, these systems are only now converging towards satisfactory solutions. The same situation may also apply to W(100)-c(2x2), Ir(110)-(1x2) and Pt(110)-(1x2): here, deeper-layer relaxations may well provide the answer, following the successful solution of the Au(110)-(1x2) structure with relaxations down to the third layer.

5. Help and Competition from Other Techniques

The issue of the excessive number of structural possibilities leads one to look for additional information about each structure, so as to narrow down the range of possibilities. Such additional information can come from other surface-sensitive techniques or from model calculations. It has repeatedly been seen that structures were solved only after the results of two or more techniques were combined, e.g. with Si(100)-(2x1) and Si(111)-(2x1).

No particular combination of two or three techniques can be singled out as being optimal for all kinds of surfaces. But it can be said that Medium- or High-Energy Ion Scattering and Scanning Tunneling Microscopy are particularly useful complements to LEED for metal and semiconductor surfaces that are clean or reconstructed or atom-covered. For atomic adsorbates SEXAFS and Angle-Resolved X-Ray Photoemission Spectroscopy (ARXPS) (including ARPEFS) have also been very powerful. For molecular adsorbates on metal surfaces, High-Resolution Electron Energy Loss Spectroscopy has been a most effective adjunct to LEED.

In some instances these alternate techniques compete with LEED in providing possibly higher accuracy in selected parameters, e.g. in substrate-adsorbate bond lengths with SEXAFS. Such results are then useful to cross-check the LEED method itself. On the theoretical side, useful cross-fertilization occurs between LEED and other techniques regarding the electron scattering process, including "fine structure" and multiple scattering.

6. Outlook

An important feature of LEED is that it is fully sensitive to atomic positions down to a depth of several layers below the surface. Thus, LEED is ideal to check whether the complete structure has been correctly solved. On the other hand, this also implies that, in a structural search, one must fit all the structural parameters essentially simultaneously. By contrast, many other techniques determine only one or two parameters at a time (e.g. the substrate-adsorbate bond length in SEXAFS), without the need to fit all other parameters, which is a much simpler problem. Another difficulty with LEED is how to improve a trial structure which has been found unsatisfactory: which parameters should be changed and in what manner so as to arrive at a more successful trial structure? This relates to the issue of conducting a structural search through a high-dimensional space of positional parameters. Apart from one promising approach [21], no efficient method to do this has been implemented so far, despite its growing importance in view of the study of increasingly complex structures: this is probably the largest problem to be resolved in LEED crystallography at present.

Another future need is the ability to perform LEED calculations for stepped surfaces with long terraces: much interesting surface chemistry and physics occur at "imperfections" such as steps. It may also be repeated that improvements in experimental techniques are desirable, in particular by the use of accurate goniometers.

On the more positive side, it should be noted that LEED in its present state is already capable of solving thousands more surface structures that have great practical value for understanding many surface phenomena. Future advances in LEED theory and experiment will amplify this trend even further.

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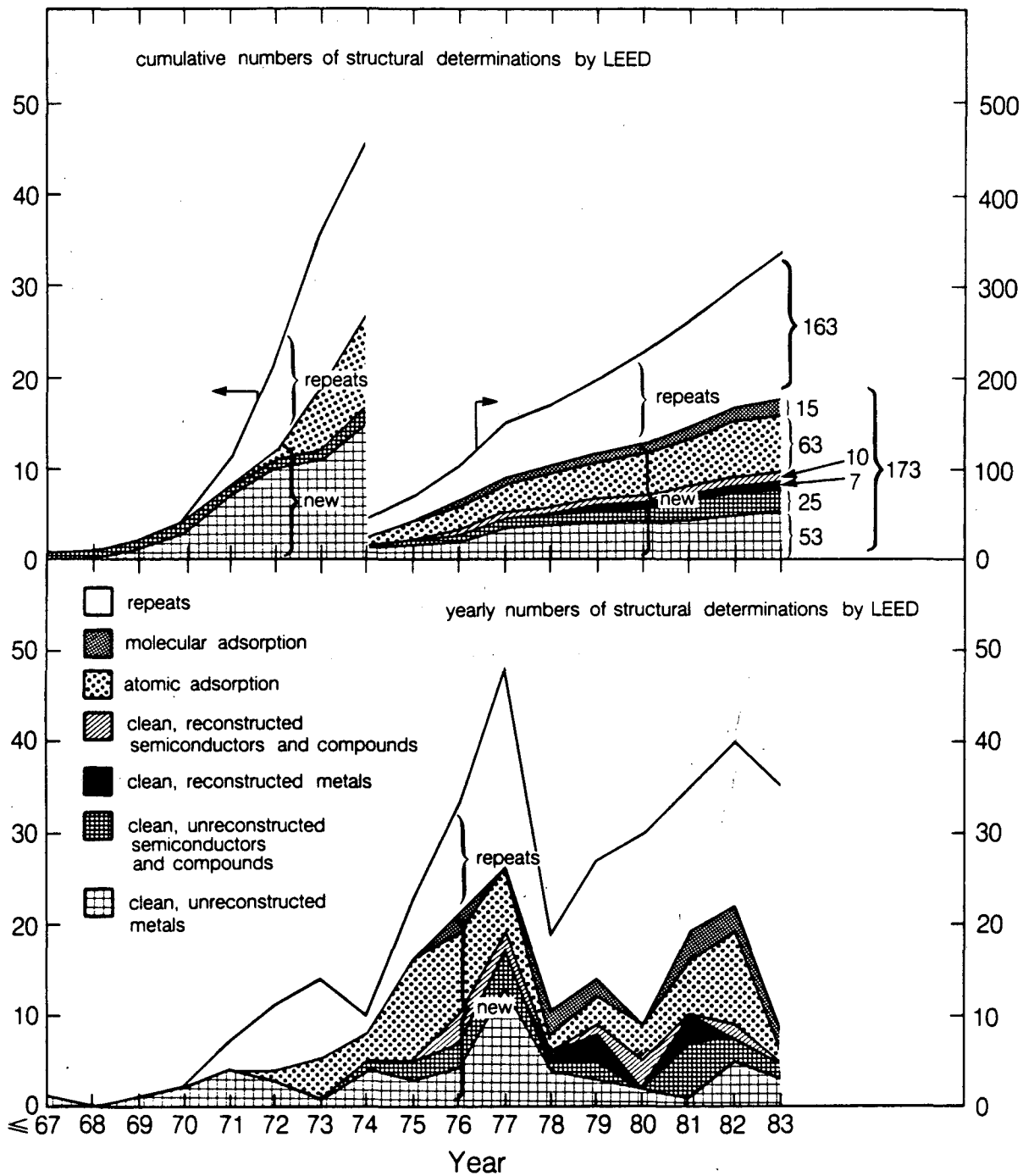
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Figure Caption

Figure 1 Yearly (bottom panel) and cumulative (top panel) numbers of structural determinations by LEED, broken up into categories of surfaces. The "repeats" include refinements of earlier analyses.



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Fig. 1

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