

Atomic-Scale Structure: from Surfaces to Nanomaterials

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This brief overview is dedicated to Professor G. Ertl's profound influence on shaping the field of surface science. I sketch recent accomplishments toward the determination and understanding of the atomic-scale structure of nanostructures. I argue that, to properly understand nanoscience and develop nanotechnology, there is a dire need to determine many more than the ~1,000 detailed surface structures known today. Techniques need to be adapted or invented to make this possible. As will be exhibited here, only two techniques are now essentially ready for this task: scanning tunneling microscopy, if interpreted by theory, and, to a lesser extent, x-ray diffraction. I also describe how low-energy electron diffraction is currently being developed for the same purpose.

Keywords: surface structure, nanostructure, nanomaterials, STM, XRD, LEED

1. Historical evolution

Arguably, surface science has been the primary origin of nanoscience and nanotechnology: after all, a distinguishing feature of nanostructures is the dominance of their surfaces and interfaces over their "bulk" or "volume". Over a period of five decades starting in the mid 1950s, surface science evolved by studying increasingly complicated types of surfaces, many properties of which are inherently nanoscale in one dimension, culminating in the study of structures with nanoscale sizes in two or three dimensions, i.e. nanowires, quantum dots, etc. [1, 2]. This evolution of surface science is graphically illustrated in Figure 1, which also shows technological drivers and scientific disciplines involved in its progression.

At the root of many properties of any kind of material is its geometric structure, especially at the atomic scale. Interatomic distances and angles dominate many phenomena, from mechanical and electronic behavior to interface magnetism and chemical reactivity. It is thus important to be able to measure such atomic-scale structure. A direct analogy can be made with materials in other fields: it is the atomic-scale structure that determines whether solids are electrical conductors, semiconductors or insulators; the atomic-scale structure of molecules has dominated the understanding of much of chemistry for a very long time; and the detailed atomic structure of proteins greatly influences progress in modern biology.

2. Comparing numbers of known structures between fields

It is instructive to push the comparison between disciplines one step further and ask how many detailed structures are known in each field, since the understanding grows with the known amount of detailed structural information. The number of known structures of inorganic solids and of molecules is, very roughly speaking, 100,000 structures each, while approximately 10,000 protein structures are known, see Figure 2: the latter number is growing rapidly thanks to x-ray diffraction using synchrotron radiation.

By contrast, the number of surface structures known with comparable detail (i.e. with bond lengths determined to about $0.01 \text{ nm} = 0.1 \text{ \AA}$ or better), is only about 1,000: this is a relatively very small database on which to build a field of materials science, especially if one considers the large number of nanostructures that are possible in principle. To produce a very rough estimate of this possible number, we may count that nanostructures containing just two elements already

can have $\sim 100 \times 100 = 10,000$ pairwise compositions (e.g. Fe and O, or Zn and S, etc.), multiplied severalfold to reflect various quantitative compositions (e.g. FeO, Fe₂O₃, Fe₃O₄, ...), then multiplied again to include different crystalline surface orientations [e.g. (100), (110), (111), ...], multiplied once more to allow for different surface concentrations of any adsorbed layers (e.g. 1, 1/2, 1/4, ... monolayers), and amplified again by the vast variety of possible adsorbates: this simple count already easily reaches well beyond the 100,000 quoted above for known bulk structures and molecules. Thus, we now know in detail less than 1% of the structures relevant to nanoscience and nanotechnology, and of the order of 1% of the number known in solid state physics and in chemistry.

Of course, theory can predict and has predicted detailed nanostructure, thanks to the large improvements in computing power and theoretical as well as computational techniques which we have witnessed in the last half century. However, theory is not a panacea, in that there exist many levels of accuracy. In particular, for complex structures approximate theoretical approaches may be chosen to keep the computation within affordable time and memory. However, the complexity of nanostructures often allows many energetically competitive structures (e.g. different particle shapes), thus requiring a higher accuracy than for simpler surface structures. It thus remains essential to cross-check theoretical predictions against experiment.

3. Techniques for surface structure determination

The scarcity of known surface structures is largely due to the experimental and theoretical difficulties of extracting that information from surfaces, let alone nanostructures. A major

contribution of surface science has been the introduction of a host of techniques that allow measuring their various properties, including atomic-scale structure. For the latter alone, many techniques are available, the major ones of which are listed in Figure 3, together with their “productivity” in terms of detailed structures solved, according to a database of solved surface structures [3].

Most productive has been the technique of low-energy electron diffraction (LEED), in which computational simulation allows fitting unknown atomic positions to measured diffraction intensities. Perhaps surprising many readers, scanning tunneling microscopy (STM), the surface science technique that started nanoscience, contributed only one result by 2003 (and a few other results more recently). This is because that database only includes “detailed” structures, with atomic positions and bond lengths determined to an accuracy of about $0.01 \text{ nm} = 0.1 \text{ \AA}$, not just parallel to the surface but also in other directions; such accuracy from STM requires a theoretical simulation with fitting of the image, analogous to the case of LEED.

We shall discuss in the following how LEED, STM and some other techniques have been or can be adapted to the detailed determination of nanostructures.

4. Techniques for nanoscale structure determination

Surface science techniques are characterized by their ability to provide sensitivity to a slice of material with nanoscale thickness on top of a single-crystal substrate. The blossoming of nanoscience and nanotechnology requires adapting or developing appropriate techniques of characterization with additional nanoscale resolution in one or two of the other dimensions. The

challenge of detailed atomic-level structure (bond lengths and bond angles) in such nanomaterials is even more formidable, especially if we wish to keep a three-dimensional spatial resolution in a single nanoparticle. A recent overview of the issues involved is available in a recent review [4], so we will only discuss the most promising techniques here, with special focus on STM and LEED since these methods are not covered in any detail in that recent review.

At present, it appears that mainly STM, XRD (x-ray diffraction) and high-energy electron diffraction are ready for the task of detailed nanostructure determination, while XAFS may provide such information in conjunction with other techniques: no other technique can at this stage, to my knowledge, find the atomic positions in an individual nanostructure with an accuracy of the order of $0.1 \text{ \AA} = 0.01 \text{ nm}$.

4.1 Scanning Tunneling Microscopy (STM)

STM unquestionable dominates the field of structural analysis of nanostructures [5]. However, a visual inspection of STM images is not sufficient to extract bond lengths and angles, except those parallel to an extended surface that provides some reference “yardstick” such as known bulk lattice constants. In fact, even in a qualitative sense, a visual inspection of an STM image is known to often give incorrect answers: to equate “bumps” in “topographic” images with atoms or even electronic orbitals has been shown in many cases to lead to gross errors of interpretation. For example, oxygen atoms often appear as dips when one expects to see bumps, as happens when they are adsorbed on various metal surfaces; this and other examples are discussed in Ref. [6]. It is safe to assume that a substantial fraction of published visual interpretations of STM images are simply wrong in some atomic-scale conclusions.

Many theoretical models of STM have been developed since the early work of Tersoff and Hamann [7, 8]. Most of the basic principles governing the current or topographic contrast recorded in an STM image are now well understood in terms of the electronic and atomic structures of both the tip and surface being probed, together with their interactions [9]. In particular, the STM tip has to be treated on an equal footing with the sample to be probed: the geometry and electronic structure of the tip can affect the image as much as the sample's properties. This becomes particularly important for nanostructures with corners and edges, which can look like tips from the point of view of the STM "tip".

A theory which has revealed itself to be computationally fast, convenient and remarkably realistic for calculating STM images is the elastic-scattering quantum chemistry (ESQC) method [10, 11, 12], in spite of the use of the simple Extended Hückel Theory (EHT) to describe the electronic structure. It has been successfully applied to a variety of surfaces, although rarely to fit unknown atomic positions to experimental images. One example of structural determination by such fitting is the case of S atoms adsorbed on Mo(100), for which the S height above the Mo substrate was obtained [13, 14]. More recently, ab initio based formalisms relying on Bardeen's approximation to the electron current have been successfully applied to semiconductor and metal surfaces [15, 16]. Such codes, however, involve large computer resources and become inefficient when dealing with complex systems for which many possible structural configurations need to be explored, especially when there is a need to simulate entire images rather than just a few scan lines.

While most STM computer codes are set up for periodic two-dimensional surfaces, their application to non-periodic systems such as nanostructures is feasible to some degree through the subterfuge of periodic boundary conditions (i.e. repeating tip-nanostructure units), thanks to the relative locality of STM tunneling. Converting periodic codes to non-periodic ones is also an option, even though this may require more computing resources.

4.2 X-Ray Diffraction (XRD)

X-ray diffraction has recently started to be applied to nanoparticles [17, 18, 19, 20, 21, 22]. Several of these studies obtain the particle shape and/or average lattice parameters, without determining local atom-by-atom deviations from such average lattice constants. The challenge with XRD is to obtain a measurable signal, usually requiring enough identical nanoparticles, thus also demanding sufficient uniformity of size and orientation.

A very successful example is the structure determination of 102-atom gold clusters, each coated in a layer of p-mercaptobenzoic acid molecules and then crystallized [19]. Their analysis revealed an unexpected chiral structure with 5-fold axial symmetry: the Au core can be viewed as five twinned face-centered cubic crystallites.

Another example concerns Co nano-islands on Cu(001) [22], for which the so-called mesoscopic misfit was investigated. The authors observe that small Co islands (1-2 nm in diameter) deposited on Cu(001) at 170 K (the total coverage is in the 0.1-0.5 ML range) show significant static disorder, i.e. many Co atoms are positioned somewhat away from the ideal hollow sites.

This is due to the fact that the Co-Co distance is observed to be sharply reduced (by up to 10%) in these islands as compared to the bulk.

4.3 X-Ray Absorption Spectroscopy (XAS)

A natural technique for investigating nanoparticles is x-ray absorption spectroscopy (XAS), including in particular extended x-ray absorption fine structure (EXAFS), and x-ray absorption near-edge structure (XANES, also called near-edge x-ray absorption fine structure or NEXAFS): this technique inherently focuses on structure around a central atom [23, 24], and is thus less dependent on periodic ordering than XRD or LEED.

One example is provided by the study of carbon-supported Pt nanoparticles in the 2-6 nm diameter range [23]. An fcc packing of the Pt atoms and a hemispherical cluster shape were in this case suggested by STEM (scanning transmission electron microscopy) and supported by the EXAFS data. Using temperature-dependent EXAFS data, it is possible to distinguish static disorder (in this case atomic relaxations from bulk-like positions) from thermal disorder (random displacements due to thermal vibrations). This provides a distribution of interatomic distances in the nanoparticles. However, it is difficult to assign specific displacements to specific atoms, so that a relatively simple model must be fit to the available data. For the smallest nanoparticles (2 nm), one model yielded an average first-nearest-neighbor distance reduced by 0.002 nm or 0.7% relative to bulk Pt and largest individual reductions about 6 times larger.

4.4 Low-energy electron diffraction and NanoLEED

LEED was developed over the last half century to measure the atomic structure of an extended surface of about a millimeter in size to a depth of about a nanometer, as given by the cross-section of the typical LEED beam and by the electron mean-free path, respectively [25]. In that well-tested and successful implementation, LEED has solved some 1000 surface structures of great variety [26]. This implementation also allows determining the structure of some nanostructures, for example C_{60} buckyballs adsorbed in a periodic (4x4) lattice on an extended Cu(111) surface [27]: as long as the nanostructure is periodic with a unit cell that is not too large, a conventional LEED analysis is possible.

A different approach for LEED would be to sample a single – and thus non-periodic – nanostructure, for instance a single nanodot, nanotube or nanowire (attached to a surface or hanging from supports). This could be achieved experimentally by narrow or focused LEED beams: two approaches have already been proposed, as discussed next.

It should be possible to focus the incident LEED beam onto a small area, as can currently be done in low-energy electron microscopy (LEEM) on the scale of 250 nm, including in future onto smaller areas. Diffraction from single objects as small as a few nanometers is conceivable. Electron beams have in fact been focused to dimensions in the 50 nm range in various applications [28]. Then the diffracted pattern can be recorded, either as angular dependent intensity data or as energy-dependent data (“I-V curves”).

This idea has been proposed theoretically in the form of convergent-beam LEED (CBLEED) [29]. The angular spread of the converging beam then implies a corresponding broadening of the

diffraction pattern. In the case of an ordered structure, the sharp spots of normal LEED would be replaced by disks delimited by the angular spread of the convergent beam: these disks contain angle-dependent intensities that provide additional structural information not present in sharp spots. Even for a diffuse LEED pattern (without sharp spots due to absence of long-range periodicity) this would still be valuable if this spread is taken into account in the calculation through convolution (as is already commonly done, for example, in photoelectron diffraction to reflect the angular aperture of the detector [30]).

Another approach is to use as electron source an STM tip located tens or hundreds of nanometers from the nanostructure; this tip serves to emit a very narrow beam with angular spread of only about 5° [31]. Such an experiment has already produced LEED patterns from areas as small as $400\ \mu\text{m}$ across, with areas smaller than $50\ \text{nm}$ across being possible.

On the theoretical side, two new features must be addressed to analyze measured LEED intensities: a convergent incident beam and the greater structural complexity of a nanostructure compared with typical periodic unit cells on an extended surface. These challenges are met in a new method, called NanoLEED, that we have implemented in recent years [32, 33, 34, 35]. In this method, a cluster model is assumed (since periodicity is not expected), in which the wavefield is expressed in terms of spherical partial waves. This then quite naturally allows the use of a convergent incident beam.

The challenge of the structural complexity of a nanostructure requires a more efficient solution of the multiple-scattering problem than available previously. I here briefly describe two

computationally efficient methods which we have developed to solve the multiple scattering problem in LEED [32, 33, 34]: an approximate grid-based method called Sparse-Matrix Canonical Grid or SMCG method; and the approximate “UV” method. Both approaches are iterative and rely in LEED on sufficient inelastic damping of electron wave amplitudes to compensate for the strong elastic scattering.

First, let’s recall that solving the multiple scattering in LEED can be formulated as the inversion of a matrix A , which involves computing times that typically scale as N^3 and N^2 , depending on the method, if A has dimension N .

In the Sparse-Matrix Canonical Grid (SMCG) method [36], the scaling is improved by the Fast Fourier Transform (FFT). This is made possible by changing matrix A to be strictly periodic (as for a periodic structure), i.e. $A_{n,m} = A_{n-m}$, even though the structure may not be periodic at all. For LEED, this requires solving the scattering as if the atoms occupied a periodic, rectangular spatial grid. With an arbitrary non-periodic structure, including any nanostructure, we can construct such a regular grid and refer each atom to its nearest grid point: then the propagation of an electron from an atom i to an atom j proceeds via the grid points P and Q nearest to atoms i and j , resp., i.e. along the path $i \rightarrow P \rightarrow Q \rightarrow j$. This method is exact if a sufficient number of partial waves are used, so as to enable the accurate propagation of electrons between each atom and its nearest grid point. The major part of the computation turns out to be the scattering between the regular grid points, which FFT solves in times proportional to $N_g \log N_g$, where N_g is the number of grid points used (in each dimension, FFT requires a number of grid points that is a power of 2): the number N_g is approximately related to the number of atoms.

An alternative method to SMCG uses Singular Value Decomposition (SVD). If the rank of matrix A (i.e. the number of its nonzero eigenvalues) is $r < N$, A can be factored into a product of three matrices, $A_{N \times N} = U_{N \times r} D_{r \times r} V_{r \times N}$, where the smaller diagonal matrix D contains the r nonzero eigenvalues of A , while U and V are rectangular. LEED does not produce vanishing eigenvalues, but this approach can still be used approximately by equating small eigenvalues to zero: we can then replace A by UDV . Thereby, the smaller is the rank r , the faster is the computation. To efficiently find the rank and the singular values of a matrix, the so-called “UV” method can be used for the SVD decomposition [37]. This approach leads to computation times proportional to $N \log N$, with N the dimension of A .

We found that the SCMG and UV methods are most efficient in different circumstances. SMCG outperforms UV for large numbers of atoms and large interatomic distances. But we also found that a more conventional approach, the Conjugate Gradient (CG) method [38], is more efficient than either SMCG or UV for small numbers of atoms and small interatomic distances [32, 33, 34]. Our NanoLEED code therefore combines these three methods and selects the most efficient one at each stage: a single structure often includes near, intermediate and distant neighbors, so different methods are applied to different pairs of atoms in the same structure.

Our implementation of these methods in the code named NanoLEED allows both periodic and non-periodic structures, including isolated nanoclusters. Two extensions have been added more recently, leading to a code named NanoTensorLEED [35]. First, we found that strong multiple scattering may occasionally cause poor convergence in NanoLEED (e.g. within a SiH_3 group,

surprisingly). To overcome this limitation, we treat such problematic small subclusters of atoms with complete matrix inversion to guarantee full and accurate inclusion of multiple scattering within them: the result is a (non-diagonal) scattering matrix describing the exact and complete scattering by that subcluster, which can then be included as a non-spherical “pseudo-atom” in the NanoLEED method. This approach uses the idea of one-center expansion applied earlier by Pendry to LEED [39] and follows the cluster approach to LEED developed in the 1980s [40].

The second extension addresses the need to automate the structural search for complex nanostructures. With such structures, we may expect to need relatively large atomic displacement steps during a search, compared to the ~ 0.01 nm steps common in past LEED searches [41]. Therefore, the second-order tensor LEED method [42] commonly used in current LEED codes [43] is likely to not be the most appropriate for nanostructures. More significantly, the conventional tensor LEED approach would be computationally much less efficient for nanostructures, because it requires one “time-reversed” LEED calculation for each exit direction: that can be done efficiently in periodic layered structures like surfaces, but not in non-periodic nanostructures. Our approach is therefore a new, simplified version of tensor LEED [44] that omits the “time-reversed” LEED calculations. This allows a more approximate but still fast estimation of the appropriate directions of displacement of the atoms; we repeat the full NanoLEED multiple-scattering calculation after each collective displacement, iterating until a minimum is found. Such an approach is analogous to the familiar use of the Hellmann-Feynman theorem in total-energy optimization [45, 46].

Our first “nanostructural” determination is currently in progress and will be reported elsewhere. In the meantime, a series of test calculations using our NanoLEED code has been performed for several types of nanostructures, including for ordered buckyballs on Cu(111) and for silicon nanowires and nanodots of various dimensions and with various deviations from the ideal bulk structure, such as different lattice terminations and surface relaxations [33, 34].

4.5. High-energy electron diffraction

Transmission electron microscopy (TEM) and high-resolution electron microscopy (HREM) can certainly image nanostructure at the atomic scale, including for single nanostructures, but do not provide three-dimensional structure. However, a closely related approach, under the name coherent electron diffraction (CED), has very recently been used to determine relaxations of the surface of single Au nanocrystals (supported by graphene) of diameter 3-5 nm [47]. Thus, the 200 kV electron diffraction pattern of a single 4 nm nanocrystal was fit with simple models of atomic relaxation, giving radial bond length contractions up to 8% relative to the interior of the particle: the larger values occur for atoms that have lower coordination, as expected.

5. Conclusions and outlook

Just as surface science required a panoply of new or adapted techniques to measure the important properties of extended surfaces, nanoscience also will benefit from novel and adapted techniques. It is also clear that, just like surface science, nanoscience must be a multi-technique field of research, in which different techniques jointly lead to the required information and understanding in order to enable further progress.

For structural determination of single nanostructures, such as with individual nanodots or nanowires, we can already use STM (interpreted by theory), XRD, CED, and to a lesser extent XAS to obtain detailed geometric structural information on the scale of $0.01 \text{ nm} = 0.1 \text{ \AA}$. LEED will also be applicable once the experimentalist can limit the incident beam to a nanoscale area on the sample; the theory is at present ready to analyze LEED intensities measured under those circumstances. LEED can already analyze, with long-established methods like tensor LEED, ordered arrays of nanomaterials of limited size, e.g. a monolayer of adsorbed buckyballs.

Only with detailed atomic-scale structural information will it be possible to bring nanoscience, and hence nanotechnology, to the level of more established sciences, such as condensed matter physics and materials science, molecular chemistry and protein biology.

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Figures

Figure 1. The historical evolution of surface science toward nanoscience in terms of types of materials studied, roughly exhibiting the increase of complexity over a period of about 50 years. Many technological drivers of the field are listed above the central arrow, while scientific disciplines that have contributed to its success are listed below the central arrow.

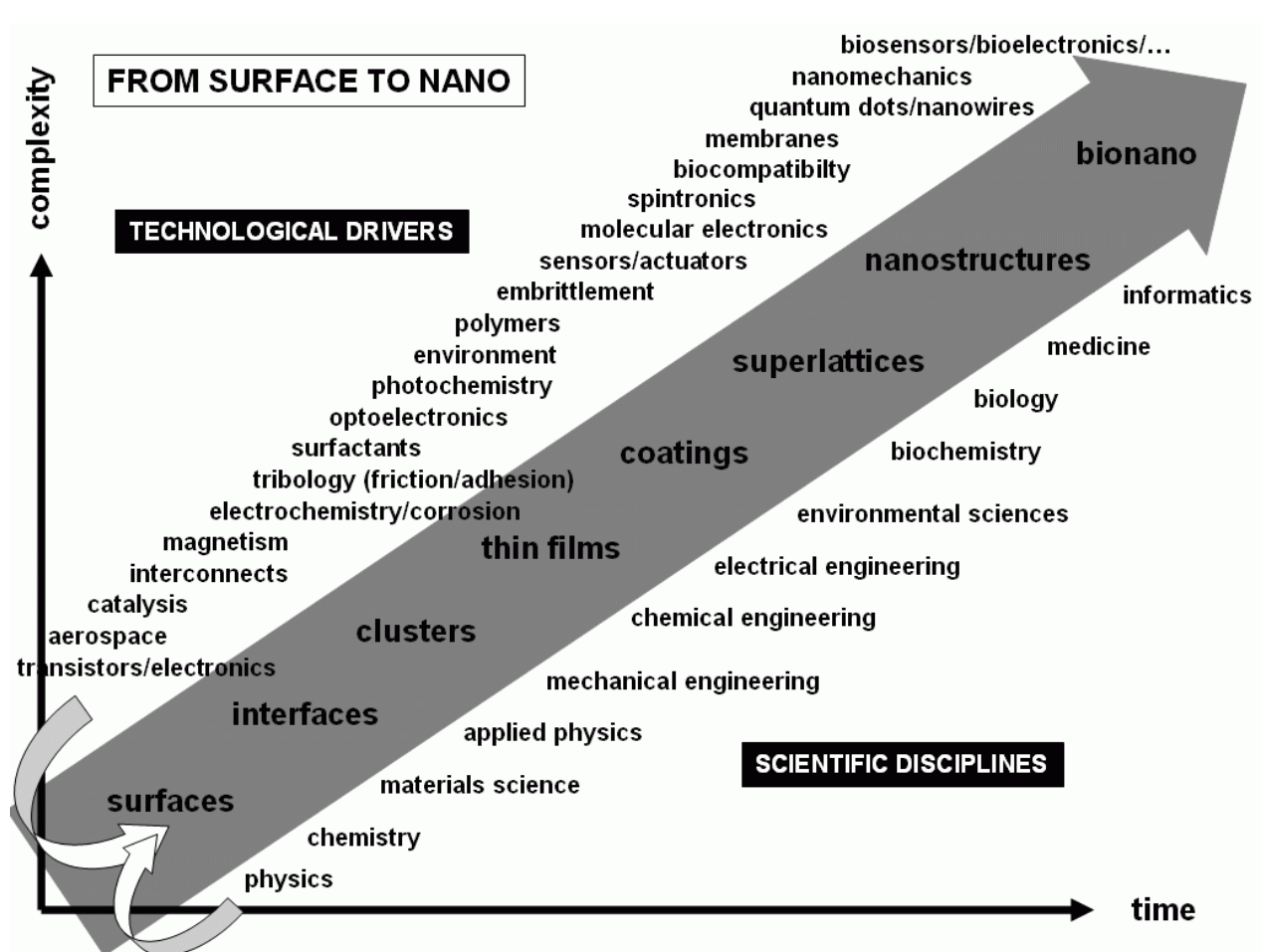


Figure 2. Comparison of numbers of detailed surface structures determined in different fields (only orders of magnitude are shown).

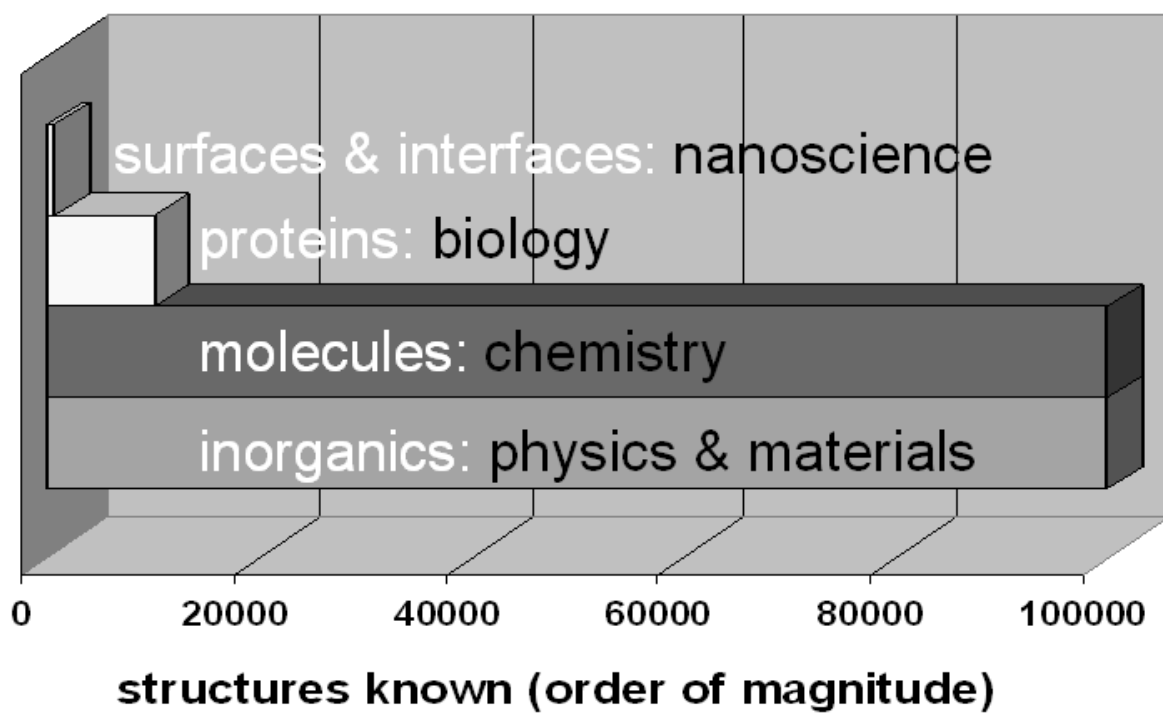


Figure 3. Graph of the number of detailed structures published before 2003, broken down by the main techniques for detailed surface structure determination, from the Surface Structure Database [1]. Some structures have been solved more than once and are multiply counted.

Acronyms: AD - atomic diffraction; AED - Auger electron diffraction; HREELS - high-resolution electron energy loss spectroscopy; IS - ion scattering; LEED - low-energy electron diffraction; LEPD - low-energy positron diffraction; MEED - medium-energy electron diffraction; NEXAFS - near-edge x-ray absorption fine structure; PED - photoelectron diffraction; RHEED - reflection high-energy electron diffraction; SEELFS - surface extended-energy-loss fine structure; SEXAFS - surface extended x-ray absorption fine structure; STM - scanning tunneling microscopy; TED - transmission electron diffraction; TOF-SARS - time-of-flight scattering and recoiling spectrometry; XRD - x-ray diffraction; XSW - x-ray standing waves.

SSD: structures by technique < 2003

