

Efficient calculation of electron diffraction for the structural determination of nanomaterials

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Abstract

A critical advance in the technique of low-energy electron diffraction (LEED) is presented and shown to enable determining detailed structures of nanomaterials, based on experimental methods that already exist or have been proposed. Our new cluster approach speeds up the computation to scale as $n \log n$, rather than the current n^3 or n^2 , with n the number of atoms, for example. Applications are illustrated for C_{60} molecules adsorbed on a Cu(111) surface, with and without co-adsorbed metal atoms, exhibiting sensitivity to important structural features such as buckyball size and deformation.

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Nanomaterials open up new fields of science and hold great promise for many novel applications^{1,2}. As in other fields, the atomic-scale structure (including bond lengths and bond angles) plays a fundamental role, especially in understanding and predicting a multitude of useful materials properties. Such information is now sorely missing, for lack of suitable techniques to obtain it from experiment.

Indeed, few techniques are currently available, and none has yet been used to our knowledge, to determine the detailed atomic-scale structure of nanomaterials from experiment with the precision needed to calculate their properties, i.e. on the scale of $0.01 \text{ nm} = 0.1 \text{ \AA}$ or better. X-ray diffraction (XRD) is a candidate for complex structures that are periodic and well-prepared³. X-ray absorption fine structure (XAFS) is much more tolerant of long-range disorder, but less capable of handling the mix of inequivalent

atomic environments typical of nanostructures⁴. Scanning tunneling microscopy (STM) provides impressive atomic-scale imaging of single nanostructures, but requires theoretical modeling to extract bond lengths and angles⁵. Theory, whether phenomenological or using first principles, can predict nanostructural details, but must itself be checked against determination from experiment.

We prove conclusively here that low-energy electron diffraction (LEED) offers great promise for the detailed structural determination of many nanomaterials. LEED experiments have already produced diffraction patterns from arrays of ordered nanoparticles, such as adsorbed buckminsterfullerenes⁶; it would be a routine matter to measure their diffracted intensities with existing equipment. For less well-ordered nanostructures, it should be possible to focus the incident LEED beam onto a single particle or small area and record the diffracted pattern, either as angular dependent intensity data or as energy-dependent data (“I-V curves”): this has been proposed in the form of convergent-beam LEED (CBLEED)⁷; diffraction from objects as small as a few nanometers is conceivable. Another approach is to use an STM tip as electron source to form a very narrow beam⁸: such an experiment has already produced diffraction patterns from areas as small as 400 μm across, with areas smaller than 50 nm across being possible in principle.

LEED also requires a theory to extract structural information, due to strong multiple scattering of the diffracted electrons^{9,10}. The multiple scattering, which can be formulated as the solution of a matrix-vector equation $Ax = b$, requires compute times that scale as

N^3 for matrix inversion or N^2 for some iterative schemes, as implemented in existing LEED codes, where the matrix dimension N is proportional to the number of inequivalent atoms n . Such power-law scaling can be very challenging for nanostructures, for which n can be in the hundreds and N in the many thousands, at least. The present work develops a theoretical scheme that scales much more favorably, namely as $N \log N$ and thus $n \log n$, making nanostructures accessible. It is a cluster approach based on mathematical methods developed in the context of the multiple scattering of electromagnetic waves^{11,12}. Our adaptation of these methods is shown here to permit the calculation of LEED intensities for representative nanostructures, for which we chose buckminsterfullerene (C_{60}) adsorbed on surfaces. By analyzing structural sensitivity, we prove that this approach can also be applied to the task of structural determination of nanostructures.

We describe three new methods to solve the multiple scattering problem: an exactly convergent method (Conjugate Gradient or CG), for reference and for greater speed compared to direct matrix inversion; an approximate grid-based method (Sparse-Matrix Canonical Grid or SMCG); and the approximate “UV” method. While these methods have been used in other contexts, it was necessary to carefully adapt them to the specific and challenging characteristics of LEED with its high angular momenta, in particular to ensure good convergence¹³.

The Conjugate Gradient (CG) method¹⁴ solves the matrix-vector equation $Ax = b$ iteratively: at each iteration step, the method uses the gradient of the right-hand side to

improve the solution. Since our multiple scattering matrix is not Hermitian, we adopt the Bi-Conjugate Gradient (BiCG) version¹⁵, which uses both $Ax = b$ and its adjoint equation. If BiCG needs N_s steps to converge and if A has dimension N , the compute time needed scales as $N_s N^2$, while the required memory scales as N^2 , compared to the inversion method's N^3 and N^2 scaling behaviors, respectively.

In the Sparse-Matrix Canonical Grid (SMCG) method¹¹, the scaling is improved by Fast Fourier Transform (FFT). If matrix A is assumed to be strictly periodic (as for a periodic structure), i.e. $A_{n,m} = A_{n-m}$, solving $Ax = b$ scales as $N \log N$ in terms of compute time. Moreover, only $2N - 1$ elements of A are distinct, significantly reducing the memory requirement. For electron diffraction, this requires that the atoms occupy a periodic, rectangular spatial grid. With an arbitrary non-periodic structure, including any nanostructure, we can still construct such a 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. Solving $Ax = b$ by BiCG now scales as $N_s N_g \log N_g$ in compute time, if N_g is the total number of grid points. The required memory only scales linearly with N_g .

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 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 Ax by $UDVx$.

Thereby, the smaller is r , the larger are the savings in computer operations. To efficiently find the rank and the singular values of a matrix, the “UV” method was proposed for the SVD decomposition¹². The resulting accuracy depends on the choice of the sampled rows and columns. Since their number can be much smaller than N , the total compute time of UV-BiCG can scale more efficiently than $N_s \times N^2$: empirically, for electromagnetic scattering, the scaling¹² is like $N_s N \log N$.

In LEED, multiple scattering is strong, due to large cross-sections, and highly anisotropic, requiring many partial waves. Adding the complexity of nanostructures, namely a large number of inequivalent atoms, and the need to search for the solution among many trial structures, therefore poses a very serious computational challenge.

The standard LEED method^{9,10} calculates matrices T_i , representing the amplitudes due to scattering paths ending at all atoms i ($i = 1, \dots, n$), including all partial waves and all multiple scattering paths within a suitably chosen cluster or layer of atoms. The matrices T_i are the solution of the equation $AT = t$, where $T = (T_1 \ T_2 \ \dots \ T_n)^T$, while $t = (t_1 \ t_2 \ \dots \ t_n)^T$ contains the known atomic scattering properties of each atom i , and $A = I - tG$ also contains the unit matrix as well as Green’s functions G for propagation between the various atoms. The dimension N of matrix A is proportional to

the number n of inequivalent atoms in the cluster or layer and to the number of partial waves needed, $L = (l_{\max} + 1)^2$, typically 25 to 100. Efficiently solving $AT = t$ for representative nanostructures is our aim here. Our implementation (in a code named nanoLEED) allows both periodic and non-periodic structures, including isolated nanoclusters.

To test our methods, we performed LEED calculations for buckminsterfullerenes (C_{60}); in fig. 1, we compare selected LEED beam intensities vs. voltage (“I-V curves”) calculated for a periodic monolayer of pure C_{60} : a well-converged CG result serves as reference for approximate SMCG and UV results, as well as a combined CG+SMCG+UV approach described below. Requiring the same number of iterations to converge as CG, the SMCG calculation used a three-dimensional grid spacing of 0.4 nm. The UV calculation neglected all the matrix elements irrelevant to the rank calculation; our procedure typically yielded ranks $\sim 17\%$ of N . We chose a realistic $l_{\max} = 7$ and inelastic potential of $V_i = -5eV$. The accuracy of the calculations is seen to yield visually indistinguishable curves. At 100 eV, our computer yielded compute times per iteration for these CG, SMCG and UV results of 252.81, 77.75 and 94.65 seconds, respectively.

We now discuss the relative performances of CG, SMCG and UV observed in our LEED tests. We find that each method outperforms the others in specific circumstances, so that a combined approach will be most appropriate.

First, SMCG is most effective in LEED for a large number of atoms, due to the fact that

the time-consuming, grid-related results are common to all atoms closest to the same grid point. Secondly, SMCG tolerates a reasonably low l_{\max} to properly describe distant atoms but needs higher l_{\max} for closely-packed atoms. Thus, SMCG outperforms CG and UV for large numbers of atoms and large interatomic distances. The accuracy of the UV method depends on the abovementioned sampling of rows and columns and does not depend on the value of l_{\max} . In the case of LEED, it is quite easy to design a suitable sampling algorithm for small matrices, corresponding to small numbers of atoms, but this topic requires more research for large matrices, i.e. for large numbers of atoms and thus more distant atoms. Consequently, UV at present works best for smaller clusters, although not as well as CG for the smallest clusters. CG is most effective for very small atom numbers and distances, such as a small cluster of close-packed neighbors. In the tested case, combining the advantages of SMCG and UV yields very precise results (see fig. 1) in 66.66 seconds per iteration.

We can exploit the relative strengths of CG, SMCG and UV by splitting the initial matrix A into three parts, $A = A_d + A_{UV} + A_{SMCG}$, each of which is then treated with a different method. Here, A_d includes close atoms only (and the unit matrix I of $A = I - tG$), which are best treated by CG; A_{UV} includes atoms with intermediate separations, best treated by UV; and A_{SMCG} includes only distant atoms, treated by SMCG. This decomposition has been used for rough-surface scattering problems under the name "UV-SMCG"¹⁶.

Consequently, the compute time per iteration has three additive components, with compute times that scale differently: for SMCG as $N_g \log N_g$, where the number of grid points N_g is normally smaller than the number of atoms in the cluster; for CG as the (relatively small) number of closest pairs of atoms; and for UV as the (also relatively small) number of UV-treated pairs of atoms. Thus the overall performance of the combined CG+SMCG+UV approach depends on the structure type. However, for large nanostructures, the SMCG part always strongly dominates, so the overall time approaches its favorable $N_g \log N_g$ scaling. For example, in the $C_{60}/Cu(111)$ test case, each iteration step was completed in 68.83 seconds: 9.20 seconds for the UV part ; 2.51 seconds for the CG part; and 57.12 seconds for the SMCG part. Figure 2 verifies that the combined method approaches the $N_g \log N_g$ scaling.

It is useful to realize that the SMCG part of the calculation, although by far the most time consuming, contributes typically only ~20% percent of the final intensity. Consequently, if we neglect that part at first and then feed the approximate result into a full-matrix calculation as an initial guess, we can save more than half of the original compute time.

A central application of LEED has been the atomic-scale structural determination of single-crystal surfaces, thanks to the high sensitivity of I-V curves to changes in atomic positions. We can now prove that this sensitivity to structure is maintained for nanostructures. For this, we tested our methods for a monolayer of C_{60} molecules, and of endohedral and exohedral C_{60} by addition of single Cu or Li atoms within and outside each C_{60} , respectively. For similarity with known structures reported in the literature⁶, we

ordered these nanostructures as adsorbates with (4x4) periodicity on a Cu(111) single-crystal substrate, the C₆₀ centers being located over hollow sites. Since the substrate lies deep under the outer surface, we included only 4 Cu layers, the number of atoms being $n = 124$ or 125 per unit cell, without or with a Li or Cu atom, respectively.

Figures 3 and 4 show I-V curves for representative diffracted beams, calculated with our new combined method. Figure 3 illustrates a very strong dependence on the C₆₀ radius, which varies in steps of $0.02 \text{ nm} = 0.2 \text{ \AA}$, while the distance between the substrate and the nearest C atoms is fixed: all beams exhibit similar sensitivity.

Figure 4 compares results with Li or Cu in three different positions consistent with normal interatomic distances, while the C₆₀ is allowed to distort by partial flattening, as a hypothetical example of a possible response to the presence of exohedral or endohedral metal.

In summary, we have adapted new efficient and accurate methods to enable LEED calculations for complex nanostructures. These methods scale as $n \log n$, rather than the current n^3 or n^2 , with the number of inequivalent atoms n . Sensitivity of the I-V curves to structural changes was proven and illustrated with LEED calculations performed for a monolayer of C₆₀ adsorbed on Cu(111). Experimental techniques necessary to perform LEED measurements on ordered nanostructures already exist. Given the satisfactory sensitivity and the efficient scaling recorded for LEED simulations, we believe that

detailed structural determination for materials with very large unit cells and for nanoclusters is now possible, a key advance for progress in nanoscience and technology.

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Figure captions:

Figure 1. Comparison of LEED intensities calculated by different methods described in the text, for a periodic monolayer of C_{60} that mimics a (4x4) layer on Cu(111), absent here, using the corresponding fractional-order beam notation, at normal incidence.

Curves are off-set vertically for clarity.

Figure 2. Actual compute times of our combined CG+SMCG+UV approach (points) for different numbers of grid points, representing larger nanoclusters, compared with a $M\log N$ extrapolation of the leftmost point.

Figure 3. As fig. 1, but including 4 layers of Cu(111) under the periodic (4x4) C_{60} monolayer. The radius of the C_{60} molecules is varied as indicated, keeping constant the spacing between the Cu and nearest C.

Figure 4. As fig. 3, but adding one atom of Li (at left) or Cu (at right) for each C_{60} molecule, in either of three positions: inside and 0.143 nm (Li) or 0.174 nm (Cu) above the center of C_{60} ("in and up"), or inside and 0.143 nm (Li) or 0.174 nm (Cu) below the center of C_{60} ("in and down"), or interstitially between C_{60} s ("out"), using realistic interatomic distances. In each case, the C_{60} sphere is flattened on the side of the nearest metal atom by reducing the perpendicular C-metal spacings by 20%.

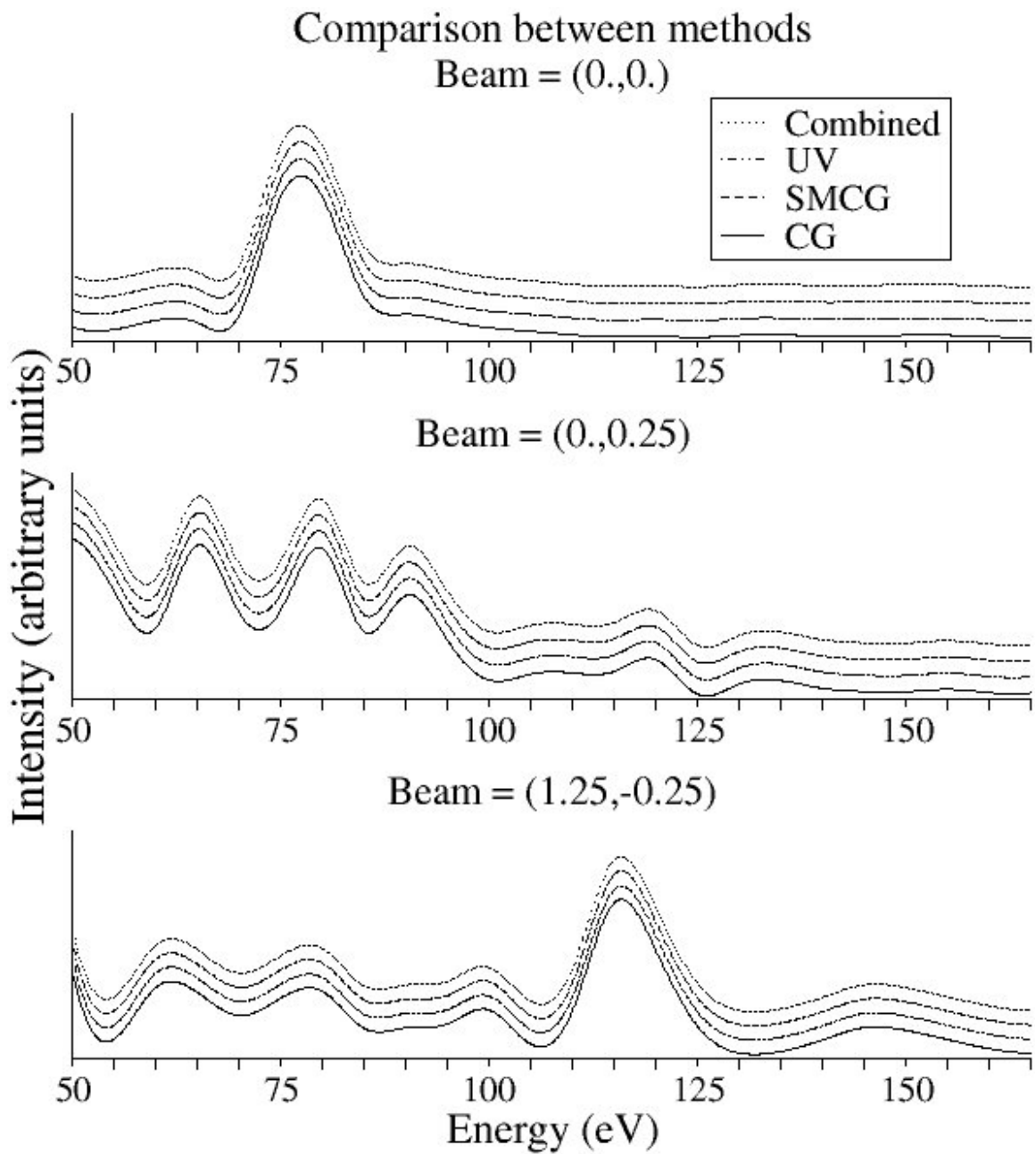


Figure 1

Compute time: scaling versus actual

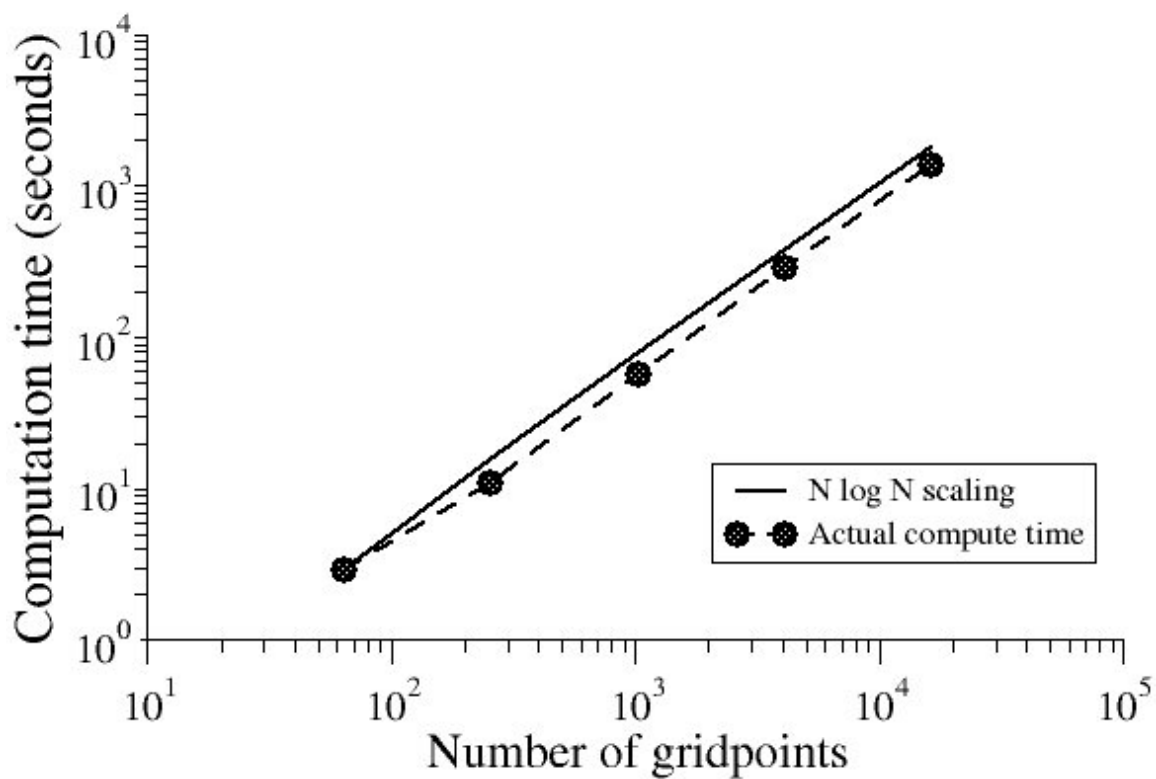


Figure 2

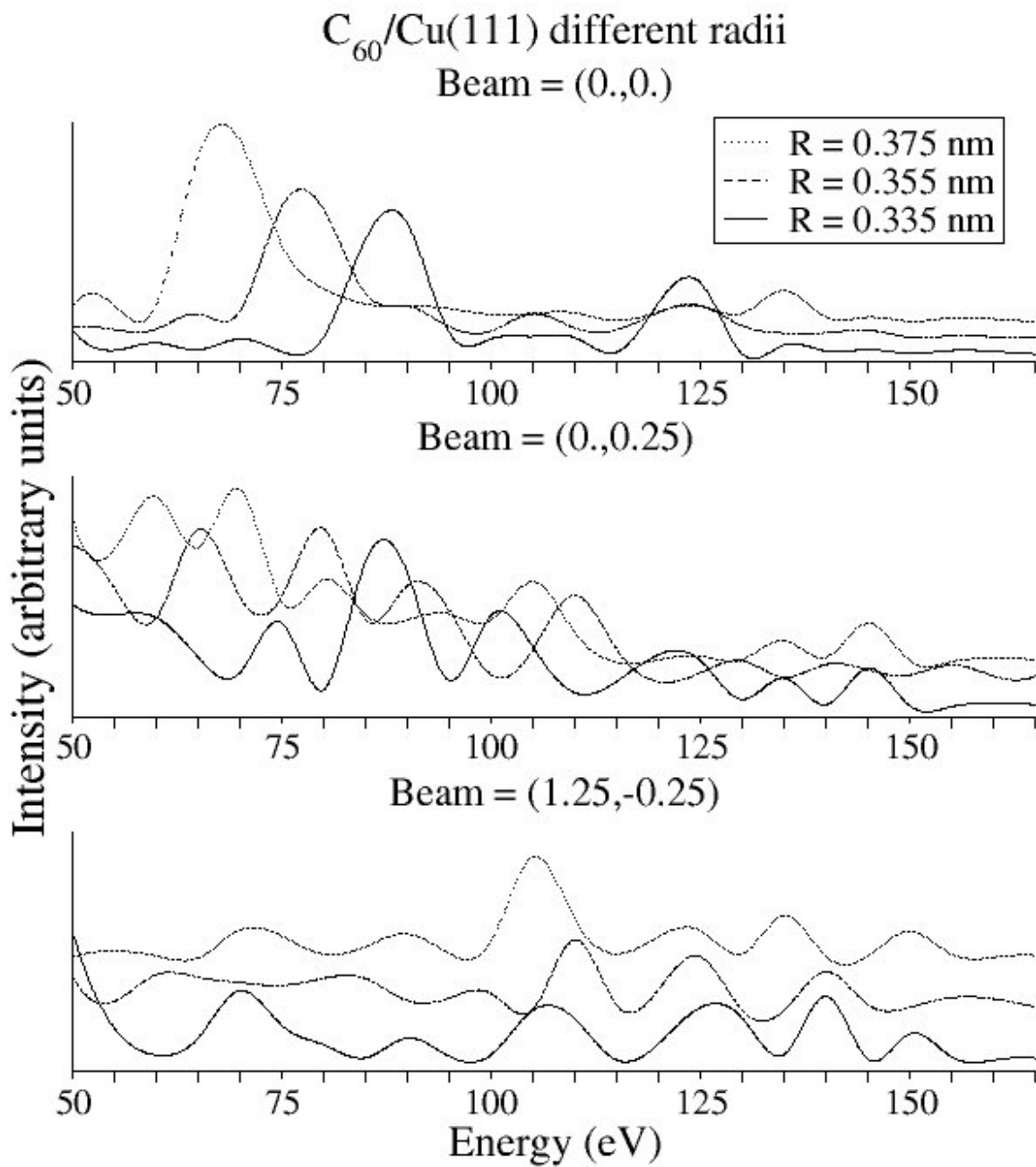


Figure 3

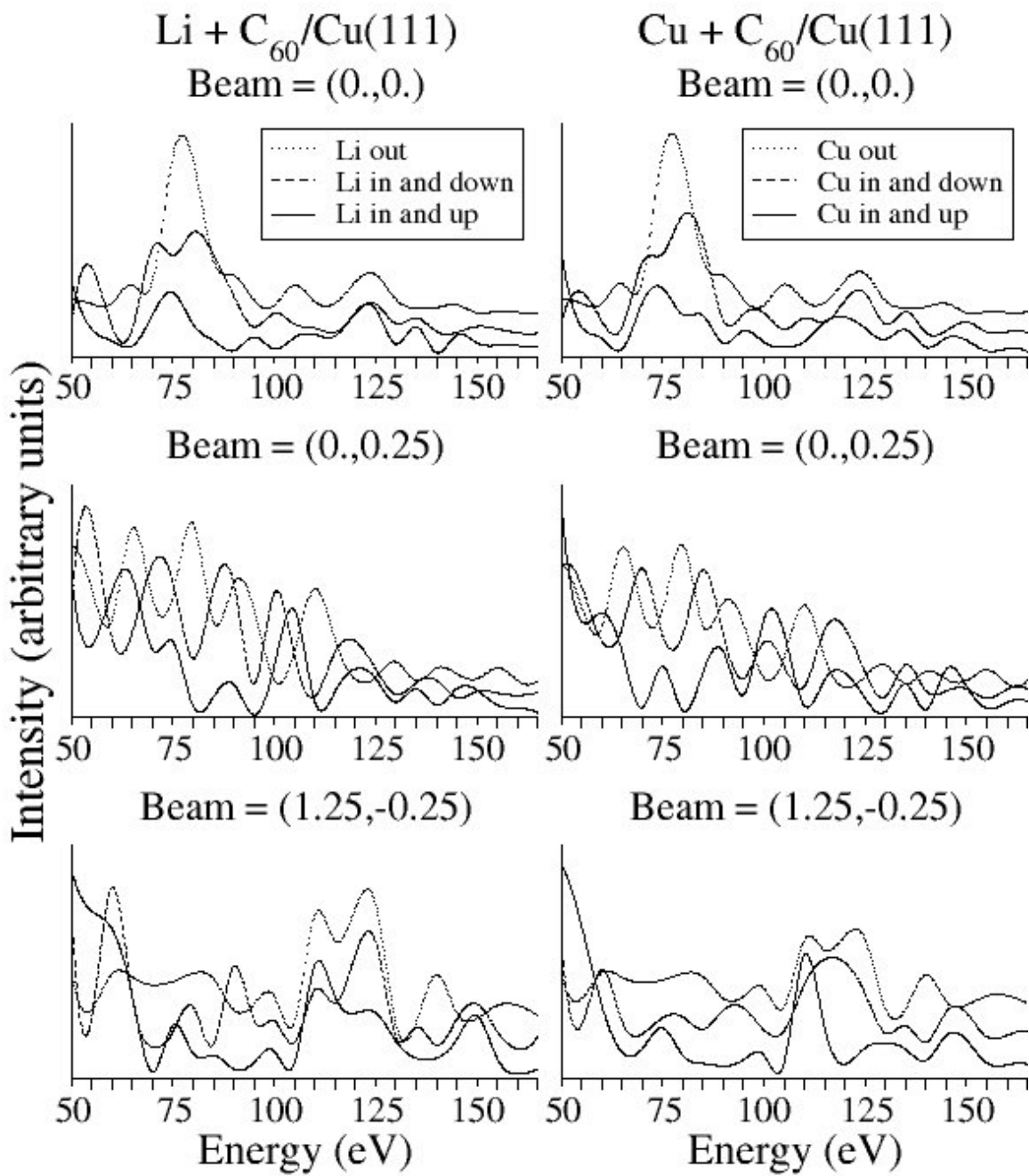


Figure 4