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Diffraction-based characterization of amorphous sp^2 carbon: sensitivity to domain-like packing of nanostructures

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We extend our method formerly suggested for structure refinement of the amorphous sp^2 carbon, based on neutron or x-ray diffraction, and applied to amorphous fullerene and its derivatives produced by vacuum annealing. To diagnose heterogeneous media, the method uses the rigid body molecular dynamics simulations of the domain-like packing for a predefined set of structural blocks. Previously, the sensitivity of the results to the variability of mutual positions of these structural blocks was analyzed in two limiting cases: (A) any domain contains only identical structural blocks and (B) all domains are the identical mixtures of many different structural blocks with variable packing of the blocks. Here, we extend this analysis to intermediate cases which correspond to domains of the type “B” with the subdomains of the type “A”. Such a structuring corresponds to a partial destruction of the nanoscale structure of the sample (e.g. by low-temperature annealing).

Keywords: neutron diffraction, computer simulation, C_{60} fullerenes, annealing, sp^2 carbon structures.

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1. Introduction

The neutron diffraction study [1] of amorphous C_{60} fullerene derivatives produced by vacuum annealing has shown the complete destruction of the initial sample structure at annealing temperatures higher than 850 °C. To obtain the quantitative characteristics of the resulting sample's structure for various annealing temperatures, one has to solve an inverse problem, which is known to be a complicated task (see e.g. [2]): the lack of spatial ordering, typical to crystalline media, leaves much freedom in the reconstruction of structural content. The widely used Reverse Monte-Carlo (RMC) method [3], applied to the structure refinement of the similar material (annealed C_{60} fullerenes) [4] enabled the authors to quantify the structure of amorphous samples in terms of the number of edges in its carbon rings. The characterization of the structure on the space scale larger than the distances between neighboring atoms was impossible because the structure, recovered by the RMC modeling, was fully chaotic on that space scale. Despite it being possible to fit the atomic pair-distribution function (or the diffraction pattern) with a model structure of carbon sample, where the order is preserved only on the space scale of the nearest neighboring atoms, the respective model structure is not a unique solution of the original inverse problem.

In [5], we suggested a method for estimating the structural properties of amorphous sp^2 carbon and applied it to the samples studied in [1]. This method enabled us to quantify the structural properties of the samples in terms of the average size and curvature of the sp^2 carbon structures (graphene-like flakes of 14 – 285 carbon atoms) as well as to estimate the fraction of the intact C_{60} fullerenes in the samples for each annealing temperature.

The main features of the method [5] are as follows: (i) we consider the fitting of the neutron or x-ray powder diffraction patterns for the scattering wave vector's modulus q in the range of a few to several tens of inverse nanometers (the inverse problems are formulated similar to that suggested in [6]); (ii) the sp^2-structured component of a sample, including the flat and curved carbon flakes with graphene-like arrangement of atoms, is described with a limited number, N_{str}, of structural blocks of a limited number of atoms, N_{atom}; (iii) the above structural blocks in a sample are packed heterogeneously, in the domains of linear size exceeding 10 nm (for q in the above-mentioned range, the interference of scattering by such separate domains may be neglected), with various average atomic density and various types of spatial ordering of structural blocks, defined by the total potential energy of the ensemble, U_{tot}; (iv) packing of structural blocks in a domain is modeled using the rigid body molecular dynamics (RBMD) [7] with the Lennard-Jones potential of atom pair interactions in the neighboring rigid-body structural blocks with variable distance R_{opt} at which the potential reaches its minimum. The simulation starts with a random distribution of blocks and the highest value of U_{tot}, and the simulation ends with an ordered steady state which naturally possesses the lowest value of U_{tot} for given initial conditions.

In [5], we interpreted the neutron powder diffraction patterns from [1] for the amorphous C_{60} fullerene obtained by mechanical grinding and subsequent annealing in vacuum at various temperatures (600, 800, 850, 900 and 1000 °C). Hereinafter, we reference the annealed samples as S_{600}, S_{800}, S_{850}, S_{900}, S_{1000}, respectively, and the un-annealed sample (i.e. after mechanical grinding only) as S_{25}. The set of the candidate structural blocks of the total number of $N_{str} = 36$ included the C_{60} fullerene molecules and the sp^2 carbon flakes with graphene-like atom arrangements of various curvatures and sizes. The sensitivity of the results to the mutual positions of these structures was analyzed in [5] in the two limiting cases: (A) any domain (taken as an ensemble ranging in number from a few dozens to several thousand nanostructures) containing only identical structural blocks (mono-structural domains) and (B) all the domains are the identical mixtures of many different structural blocks with the structural content of blocks taken from the solution of the inverse problem in the case "A" (multi-structural domains). All the domains in both cases, "A" and "B", have multiple variants of number of N_{var}, which are generated by the variance of the R_{opt} value (which determines the average density of atoms in the domain) and of the U_{tot} value (which determines both the density and the mutual spatial orientation of structural blocks). The total number of different domains to calculate in the case "A" is equal to $N_{str} \cdot N_{var}$ and N_{var}, in the case "B" (because the structural content of blocks for the multi-structural domains "B" is taken from the solution of the inverse problem in the case "A"). The results for the S_{800}, S_{850}, S_{900} and S_{1000} samples were insensitive to the types of the domains (i.e. the theoretical diffraction pattern in the case "B" fits the experimental one almost as good as in case "A"). At low values of q (< 25 nm^{-1}), fitting of the diffraction patterns for the S_{25} and S_{600} samples in the case "A" was significantly better than that in the case "B".

Here, we extend our analysis to the intermediate cases that correspond to the type "B" domains with type "A" subdomains. Such a domain-like structuring enables us to analyze the difference of inverse problem solutions in cases "A" and "B" for the S_{25} and S_{600} samples from [1].

2. Sensitivity of characterization to domain-like packing of nanostructures

In [5], we found that the fraction of carbon atoms, which belong to the intact C_{60} fullerenes, in the total number of carbon atoms (we excluded the contribution of gas impurities of N, O and H from our quantitative analysis) in the S_{25} and S_{600} samples is equal to 59 % and 49 %, respectively. For the samples annealed at high temperatures, this fraction is significantly lower. We suggested that the poor fitting of diffraction patterns for the S_{25} and S_{600} samples in the case "B" (multi-structural domains) is caused by the structuring peculiarities of the intact C_{60} fullerenes when their fraction is high. The approach in [5] implies a uniform random distribution of structural blocks in the domain's volume (and thus in the entire sample) on the space scale of a few-several nanometers. The clustering of structural blocks of the same kind, that can produce a mono-structural subdomain during the RBMD simulation of multi-structural domains, is not possible in the case of such a short-range potential as the Lennard – Jones ones. All the structural blocks from the predefined set, except the C_{60} fullerenes, have the similar structure: carbon flakes of 14 – 285 atoms with a graphene-like atom arrangement. Even if we assume that the samples actually contain the mono-structural domains of some of these structural blocks (except the C_{60} fullerenes), it would be impossible to determine this from the diffraction data only. The latter was proven in [5] for the samples annealed at high temperatures: the theoretical neutron diffraction patterns, calculated in the mono-structural and multi-structural domain cases, appeared to be identical. However, for the samples S_{25} and S_{600} with a high fraction of intact C_{60} fullerenes, the situation is different.

The easiest way to identify the presence of the mono-structural C_{60} fullerene domains in the samples S_{25} and S_{600} is to fit the experimental diffraction patterns with the calculated ones for the multi-structural domains of the sp^2 carbon flakes and mono-structural domains of the C_{60} fullerenes. Since we use the structural content of blocks found in the case of the mono-structural domains, the number of domains in the latter case is equal to $N_{var}(\text{flakes}) + N_{var}(C_{60})$. In [5], it was enough to simulate $N_{var} = 12$ variants of mono- or multi-structural domains (4 different values of R_{opt} parameter and 3 different values of U_{tot} parameter), thus $N_{var}(\text{flakes}) = 12$. For the mono-structural C_{60} fullerene domains, it is enough to model only $N_{var}(C_{60}) = 4$ variants, because, in the case of spherical molecules, the U_{tot} parameter will affect only the mutual orientation of the neighboring fullerenes, that should be taken random to allow for the effects that are visible on the diffraction patterns and caused by thermal rotation of fullerenes. In Figs. 2, 3 and 4, the calculations for this structure of the sample is labeled as "mono (C_{60}) + multi (flakes)".

Another way is to introduce manually the mono-structural subdomains of the C_{60} fullerenes into the multi-structural domains. In this case, the subdomains should be calculated separately and then introduced into the RBMD simulation of multi-structural domains as rigid bodies in order to prevent subdomain breakdown during the RBMD simulation. Fig. 1 shows the example of the calculated multi-structural domains for $\sim$ 25000 carbon atoms that include the C_{60} fullerenes subdomains of different sizes. The content of the structural blocks in these domains is taken as that obtained in [5] for the S_{600} sample (note that this structural content differs from that for the S_{25} sample) and includes (besides the intact C_{60} molecules) the decomposition products of C_{60} molecules in the amount indicated in the Fig. 1 caption. The domains in Fig. 1 are calculated with the R_{opt} parameter value which, for each pair of structures in the ensemble, is set as random in the range: 0.35 – 0.4 nm. These domains have the lowest value of U_{tot} for given R_{opt} (i.e. correspond to the final time step of RBMD simulation). We also calculated the domains for the following ranges of R_{opt}: 0.25 – 0.3, 0.3 – 0.35, 0.4 – 0.45 nm, for higher values of U_{tot} that correspond to the intermediate stages of the RBMD simulation. The total number of the calculated domains for each size of the C_{60} subdomains and for each sample is equal to $N_{var} = 12$. Depending on the relative size of the C_{60} subdomains these model samples are labeled in Figures 2, 3 and 4 as follows: "sub XL", for extra-large subdomains (see Fig. 1 (a)); "sub L", for large subdomains (see Fig. 1 (b)); "sub M", for medium subdomains (see Fig. 1 (c)); "sub S", for small subdomains (see Fig. 1 (d)). The number of C_{60} molecules in each type of subdomain is shown in the captions of Fig. 1 for the S_{600} sample and Fig. 2 for the S_{25} sample. The distances between the C_{60} molecules in the subdomains are different for different values of R_{opt}; this affects the linear sizes of the subdomains. The linear sizes of the subdomains for the R_{opt} = 0.35 – 0.4 nm are approximately 7.5 nm, 5.8 nm, 4.8 nm, 3.8 nm for "sub XL", "sub L", "sub M" and "sub S" subdomains respectively. Note, that the sizes of the simulated domains were taken to be large enough ($\sim$ 25000 atoms) to avoid disturbance of the diffraction patterns at $q > 5$ nm^{-1}, i.e. in the region that is under consideration both in [5] and here. Therefore, no periodic boundary conditions are needed.

Figures 2 and 3 show the results of fitting (by solving the inverse problem (2) – (5) in [5]) the experimental diffraction pattern with theoretical simulations for the S_{25} and S_{600} samples, respectively, for various sample structural contents. The curves for mono-structural (labeled as "mono") and multi-structural (labeled as "multi") domains are taken from [5], while the other curves are new. Figs. 2 and 3 show that it is possible to fit the experimental data in the case of mono-structural domains of the C_{60} fullerene and the multi-structural domains of the sp^2 carbon flakes almost as good as in the case of mono-structural domains.

Figure 4 shows the quality of the fitting for different cases in terms of the normalized values of the optimal objective function which describes the difference between the experimental and theoretical data (i.e. the residual, see Eqs. (2) – (5) in [5]). The case of mono-structural domains ("mono") has the lowest residual among all cases. This is not surprising, because in this case, the solver tries to fit the data with $N_{str} \cdot N_{var} = 432$ calculated curves. The case of mono-structural domains of the C_{60} fullerene and the multi-structural domains of the carbon flakes ("mono (C_{60}) + multi (flakes)") holds for the second S_{25} and the third S_{600} samples. In this case, the solver tries to fit the data with just 16 calculated curves. The case of multi-structural domains that include the relatively small C_{60} fullerene subdomains ("sub S") holds for the third S_{25} sample and for the second S_{600} sample. Only 12 curves are used in this case to fit the data. Among four variants of subdomains size, the smallest size provides the best fitting.

From this analysis, we can conclude that the partial destruction of the nanoscale structure of the amorphous C_{60} fullerene sample, resulted from the low-temperature annealing in vacuum, appears to be heterogeneous on the nanoscale. Not only do individual C_{60} molecules survive the annealing at 600 °C, but their clusters of a size of few nanometers also remain intact.

3. Conclusion

The structure refinement method [5] formerly suggested for characterization of amorphous sp^2 carbon, based on the neutron or x-ray diffraction, and applied to amorphous fullerene and its derivatives produced by vacuum annealing [5], has been extended to analyze the partial destruction of a sample's nanoscale structure (e.g. by the low-temperature annealing). To evaluate heterogeneous media, the method uses rigid body molecular dynamics simulations of the domain-like packing of the predefined set of the structural blocks. Previously, the sensitivity of the results to the variability of mutual positions of these structural blocks has been analyzed in the two limiting cases: (A) any domain containing only identical structural blocks and (B) all the domains are the identical mixtures of many different structural blocks with variable block packing. The extension of this analysis to the intermediate cases that correspond to type "B"

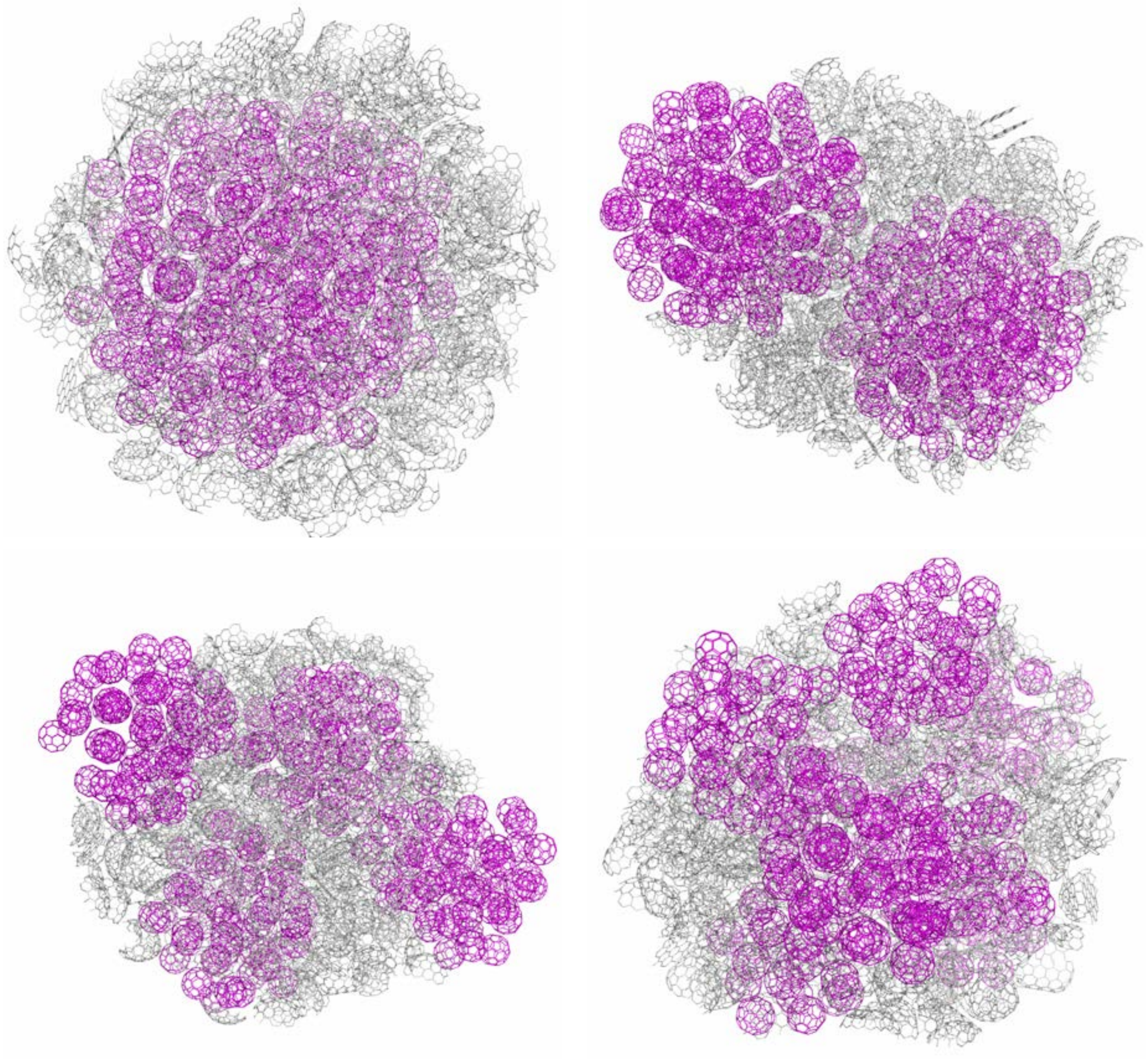

FIG. 1. The model multi-structural domains of $\sim$25000 carbon atoms of the following structural content: 49 % C_{60} fullerenes and 51 % products of decomposition of C_{60} in the form of sp^2 carbon flakes (27 % C_{58} molecules, 16 % C_{52} molecules, 6 % C_{34} molecules and 2 % C_{14} molecules). The C_{60} fullerenes are present in these domains in the form of subdomains (highlighted) of different size: one subdomain with 205 molecules (a), two subdomains with 102 – 103 molecules (b), four subdomains with 51 – 52 molecules (c), and eight subdomains with 25 – 26 molecules (d)

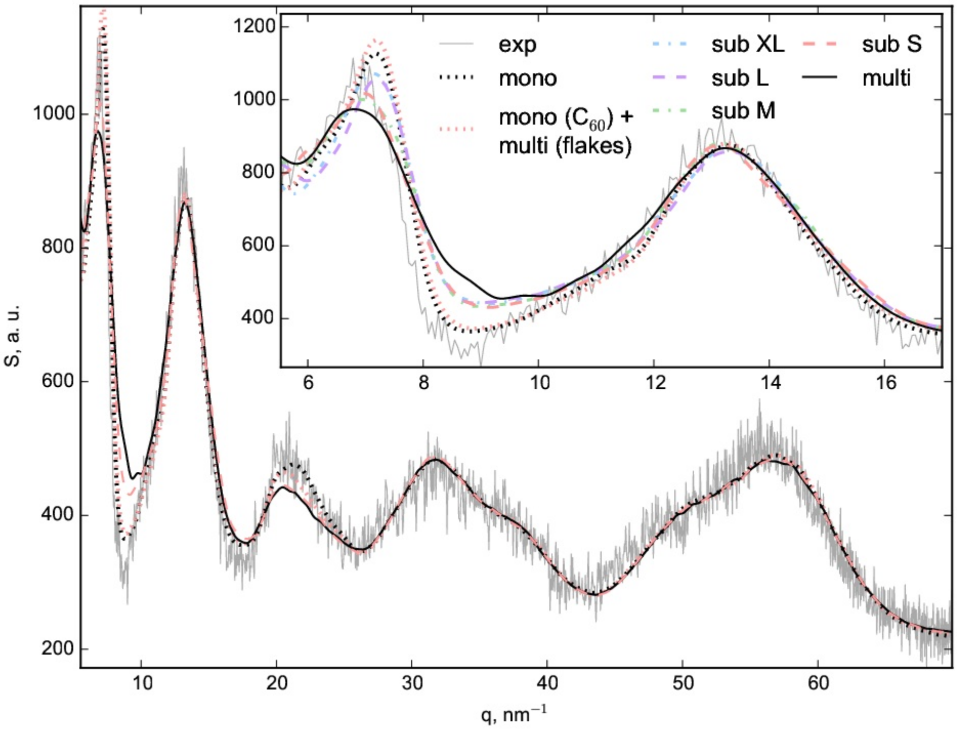

FIG. 2. Fitting of the experimental (“exp”) diffraction pattern for the un-annealed sample (S_{25} sample) with theoretical simulations, in various cases of sample’s structural content: mono-structural domains (“mono”); mono-structural domains of the C_{60} fullerene and the multi-structural domains of the sp^2 carbon flakes (“mono (C_{60}) + multi (flakes)”); multi-structural domains (“multi”); multi-structural domains that include the C_{60} fullerene subdomains of different size: extra-large (as in Fig. 1(a) but for 247 molecules, “sub XL”), large (as in Fig. 1(b) but for 123 – 124 molecules, “sub L”), medium (as in Fig. 1(c) but for 61 – 62 molecules, “sub M”), small (as in Fig. 1(d) but for 30 – 31 molecules, “sub S”). The inset magnifies the results in the range of q values from 5.5 to 17 nm^{-1}. The curves labeled with “sub XL”, “sub L”, and “sub M” are shown in the inset only to ease the readability of the main plot

domains with type “A” subdomains enables us to improve the quantitative description of the structure for amorphous C_{60} samples after the mechanical grinding and subsequent annealing at 600 °C. The partial destruction of the nanoscale structure of the amorphous C_{60} fullerene sample, resulted from the low-temperature annealing in vacuum, appears to be heterogeneous on the nanoscale. Not only do the individual C_{60} molecules survive the annealing at 600 °C, but their clusters of a size of few nanometers also remain intact.

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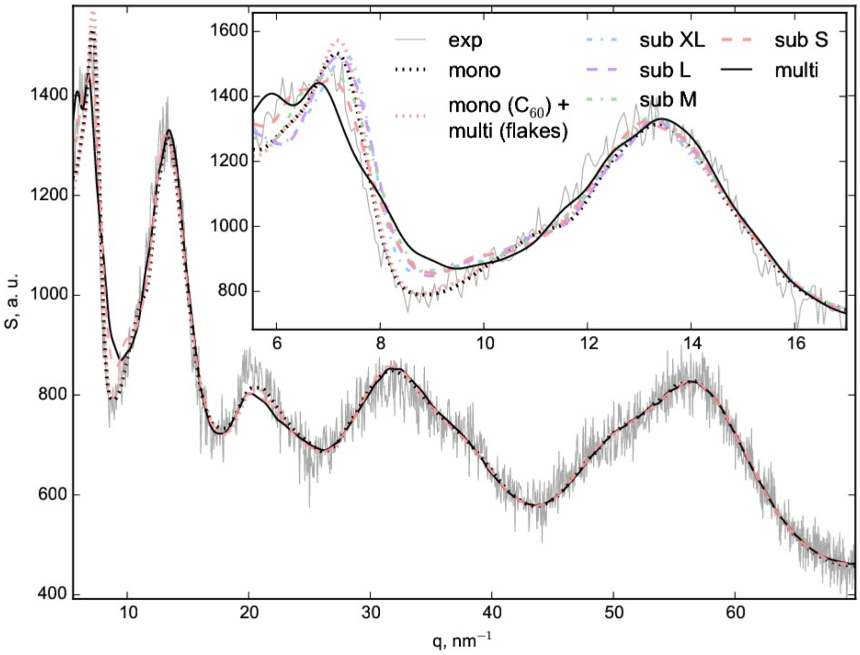

FIG. 3. The same as in the Fig. 2 but for the sample annealed at 600 °C (S_{600} sample). The parameters of the C_{60} subdomains are indicated in the caption of Fig. 1

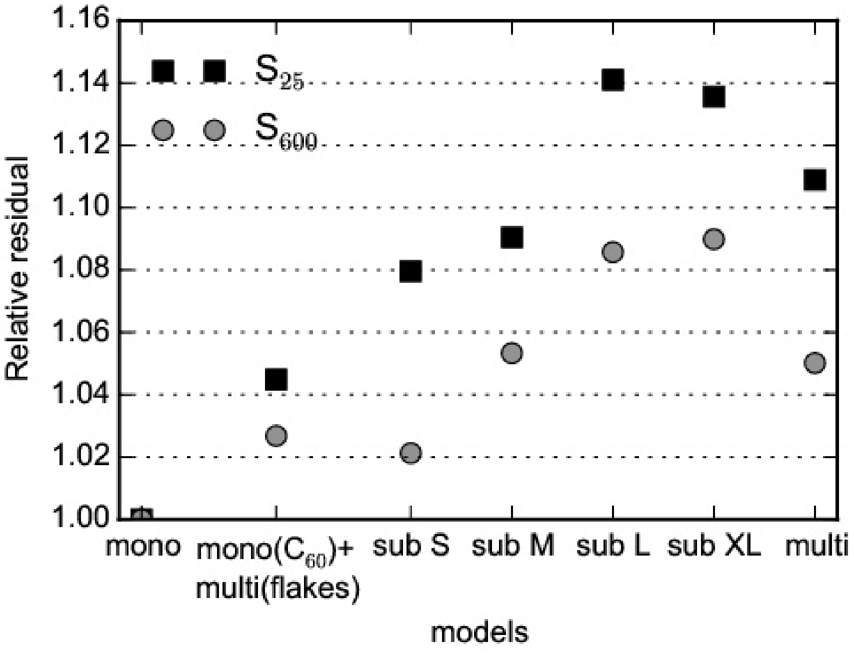

FIG. 4. Normalized values of the optimal objective function (i.e. relative residuals, see Eq. (2) – (5) in [5]) that characterize the quality of fitting the experimental diffraction patterns in different cases of the sought-for structural content of the two analyzed samples. The values are normalized to the minimum, which for both samples is found in the case of mono-structural domains (“mono”). See the caption of Fig. 2 for the annotations

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