Multilayer Diffraction Reveals That Colloidal Superlattices Approach the Structural Perfection of Single Crystals

Stefano Toso¹,²,†, Dmitry Baranov¹,†,*, Davide Altamura³, Francesco Scattarella³, Jakob Dahl⁴,⁵, Xingzhi Wang⁴,⁵, Sergio Marras⁶, A. Paul Alivisatos⁴,⁵,⁷,⁸, Andrej Singer⁹, Cinzia Giannini³,*, Liberato Manna¹,*

¹Nanochemistry Department, Istituto Italiano di Tecnologia, Via Morego 30, 16163, Italy
²International Doctoral Program in Science, Università Cattolica del Sacro Cuore, 25121 Brescia, Italy
³Istituto di Cristallografia - Consiglio Nazionale delle Ricerche (IC-CNR), via Amendola 122/O, I-70126 Bari, Italy
⁴Department of Chemistry, University of California Berkeley, Berkeley, CA, USA
⁵Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA, USA
⁶Materials Characterization Facility, Istituto Italiano di Tecnologia, Via Morego 30, 16163, Italy
⁷Department of Materials Science and Engineering, University of California Berkeley, Berkeley, CA, USA
⁸Kavli Energy NanoScience Institute, University of California Berkeley and Lawrence Berkeley National Laboratory, Berkeley, CA, USA
⁹Department of Materials Science and Engineering, Cornell University, Ithaca, New York 14850, United States

†S.T. and D.B. contributed equally.
*Corresponding authors: dmitry.baranov@iit.it, cinzia.giannini@ic.cnr.it, liberato.manna@iit.it

**ABSTRACT:** Colloidal superlattices are fascinating materials made of ordered nanocrystals, yet they are rarely called “atomically precise.” That is unsurprising, given how challenging it is to quantify the degree of structural order in these materials. However, once that order crosses a certain threshold, constructive interference of X-rays diffracted by the nanocrystals dominates the diffraction pattern, offering a wealth of structural information. By treating nanocrystals as scattering sources forming a self-probing interferometer, we developed a multilayer diffraction method that enabled the accurate determination of nanocrystal size, interparticle spacing, and their fluctuations for samples of self-assembled CsPbBr₃ and PbS nanomaterials. The average nanocrystal displacement of 0.32-1.4 Å in the studied superlattices provides a figure of merit for their structural perfection and approaches the atomic displacement parameters found in traditional crystals. The method requires a laboratory-grade diffractometer and an open-source fitting algorithm for data analysis, providing a competitive alternative to resource-intensive synchrotron experiments.
INTRODUCTION

X-ray diffraction is one of the most widespread approaches to the characterization of nanomaterials.\textsuperscript{1-3} Specifically, grazing-incidence small- and wide-angle X-ray scattering\textsuperscript{3-9} are commonly used to study the structure of colloidal nanocrystal superlattices. However, those techniques require specialized equipment such as synchrotrons and customized data-analysis algorithms, often tailored to the specific sample.\textsuperscript{8,10} Transmission electron microscopy is an accessible alternative, but it is limited to thin superlattices deposited on grids.\textsuperscript{11,12} At the same time, the periodic structure of superlattices offers the opportunity of exploiting X-ray interference to perform accurate structural refinements. Here, we introduce a multilayer diffraction method for the precise structural characterization of nanocrystal superlattices, building upon the pioneering studies on epitaxially-grown multilayer films from the 1970s.\textsuperscript{13-17}

Bragg peaks of nanocrystal superlattices feature a characteristic fine structure, that is commonly observed but seldom commented in diffractograms of lead-halide perovskite nanocrystals.\textsuperscript{18-20} In fact, the origin of this structured profile was first recognized in out-of-plane diffraction patterns of CsPbBr\textsubscript{3} superlattices.\textsuperscript{21} All nanocrystals within a superlattice diffract X-rays at the same Bragg angles, acting as orientation-selective light sources. The superlattice periodicity introduces a phase modulation on the diffracted X-rays, causing an additional interference which in turn produces the fine structure. Like an interferometric measurement, the resulting diffraction pattern contains information about the interferometer geometry, represented by the superlattice (periodicity, interparticle distance, stacking disorder), and its light sources, which are the nanocrystals (size, size distribution, atomic planes periodicity). Fitting a single diffractogram with a multiparametric model enables measurement of all these parameters with high accuracy, and represents the core of the multilayer diffraction method.

Here, the developed method was applied to the structural refinement of a variety of superlattices made of CsPbBr\textsubscript{3} and PbS, nanocrystals and nanoplatelets (Table 1). The structural characterization of CsPbBr\textsubscript{3} nanocrystal superlattices is particularly relevant due to the recent reports of their collective excitonic properties.\textsuperscript{22,23} For this reason, results were validated by comparison with the structural analysis performed by grazing-incidence diffraction techniques and electron diffraction. Once validated, the multilayer diffraction method was applied to study the evolution of the superlattice structure upon thermal annealing in the range of 25-125 °C, which was characterized by an increase in the superlattice crystallinity along with the nanocrystal lattice expansion and superlattice periodicity contraction, further showcasing its versatility.

The multilayer diffraction method is very sensitive to the stacking order of nanocrystals. We measured nanocrystal displacement parameters of 0.32-1.4 Å, an order of magnitude smaller than those reported for other colloidal superlattices by grazing incidence techniques (∼5-10 Å).\textsuperscript{8,10} These values are significantly smaller than a nanocrystal unit cell and match the periodicity fluctuations reported for epitaxially grown multilayers.\textsuperscript{16,24} The ability to self-assemble nanomaterials with such precision effectively closes the accuracy gap between wet-chemistry and physical methods. Moreover, such small fluctuations are comparable to the atomic displacement parameters found in some metalorganic bulk crystals, prompting us to reconsider nanocrystal superlattices as hybrid organic-inorganic single crystals rather than simply ordered aggregates of particles.
Figure 1. CsPbBr$_3$ nanocrystal superlattices. a) CsPbBr$_3$ superlattices grown on a silicon substrate, optical microscopy image. b) HR-SEM imaging of a superlattice surface, where the squared packing of nanoparticles is apparent. Inset: the simple-cubic structure adopted by superlattices, with its unit cell (one nanocrystal plus one organic layer in each spatial direction) outlined by a red frame. c) $\theta$:2$\theta$ out-of-plane XRD pattern of CsPbBr$_3$ superlattices plotted on a linear intensity vs. scattering vector scale and divided into three sections: low-angle ($q<0.8$ Å$^{-1}$), first Bragg peak ($q=0.8$-1.4 Å$^{-1}$), and second Bragg peak ($q>1.4$ Å$^{-1}$). Insets show the plot on a logarithmic scale, to highlight the fine structure features of the pattern. The two small peaks at $q = 0.9$-1.8 Å$^{-1}$ were assigned to an unidentified impurity. A schematic representation of how the diffraction experiment perceives the superlattice in each region: d) as an electron density square wave at low angles due to the alternation of inorganic cores and organic spacing, e) as a vertical stacking of atomic planes at the first Bragg peak, and f) as a group of isolated nanocrystals at the second Bragg peak.
RESULTS AND DISCUSSION

Superlattice Interference and Multilayer Diffraction. In our previous work on lead-halide perovskite nanocrystal superlattices we reported some unusual modulations of the Bragg peaks, here called superlattice fringes, which were absent in patterns of randomly oriented particles and arose from the mesostructure periodicity. The fringes were further exploited to estimate the structural periodicity and track its evolution in mixed-halide CsPbBr$_{13-x}$I$_x$ superlattices upon light-induced iodine sublimation, demonstrating their potential for the in-situ investigation of nanocrystal superlattices. That background established CsPbBr$_3$ superlattices as a testing ground to develop a versatile tool for the quantitative structural analysis of colloidal nanocrystal superlattices. Those 3D assemblies of cuboidal particles are grown on a flat silicon substrate (Figure 1a) and feature a simple-cubic nanocrystal packing, evidenced by HR-SEM (Figure 1b). When probed via a θ:2θ out-of-plane diffraction scan (commonly named θ:2θ XRD), they produce a pattern which is rich in complex features, better highlighted when plotted as X-ray scattering intensity on a logarithmic scale vs scattering vector modulus ($q = 4\pi \sin(\theta)/\lambda_{\text{x-ray}}$, Figure 1c).

The θ:2θ diffraction pattern can be divided into three regions: low-angle reflectivity ($q<0.8$ Å$^{-1}$), first Bragg peak ($q\approx0.8-1.4$ Å$^{-1}$) and second Bragg peak ($q>1.4$ Å$^{-1}$), each of them containing information about the superlattice structure (Figure 1d-f). The first Bragg peak region is the most interesting from the analysis point of view, as it merges the information content from both low-angle and second Bragg peak regions (mesostructure and nanocrystal atomic lattice respectively, see SI, section S.a). Upon close inspection, the first Bragg peak is composed of multiple narrow fringes (“\n” in Figure 1c) enveloped by a broader profile. Such peak shape is new to colloidal superlattices, but is often encountered in X-ray diffraction patterns of periodic multilayer films grown by physical methods. The analogy between nanocrystal superlattices and epitaxial multilayers is consistent due to a characteristic of the θ:2θ XRD geometry: the scattering vector remains perpendicular to the substrate throughout the experiment. Since diffraction occurs between objects (atomic planes and nanocrystals) stacked along the same direction, we could approximate superlattices as vertically stacked crystalline slabs separated by a gap and neglect the horizontal texture of those planes. The resulting multilayer diffraction method is an adaptation of a model published in 1991 by Fullerton et al. for physically grown multilayers. Below, we outline the physical picture and present the structural parameters considered by the model, while its full description is provided in Sections S.b-j of the SI.

When X-rays hit the superlattices, they are first diffracted by atomic planes within individual nanocrystals, which in turn act as diffraction gratings. Each nanocrystal produces a diffraction profile with intrinsic size broadening (nanocrystal form factor), shaped as a broad peak with weak side ripples (Figure 2a). The position and breadth of the nanocrystal form factor depend on the interplanar periodicity $d$ and number of scattering planes $N$, respectively. Following this diffraction event, the superlattice periodicity $\Lambda$ introduces a q-dependent phase mismatch between radiation coming from different nanocrystals, forming interference fringes. In this respect, superlattices behave as self-probing interferometers where nanocrystals serve as orientation-selective secondary light sources accurately measuring their own relative distances. The stacking periodicity $\Lambda$ is defined as the sum of the nanocrystal thickness (a function of $d$ and $N$) plus the interparticle spacing $L$, according to the equation $\Lambda = d \cdot (N - 1) + L$. In the case of a perfect superlattice, the diffraction profile would be that shown in Figure 2b. However, superlattices contain two kinds of disorder: a continuous disorder due to the fluctuation of the interparticle spacing, and a discrete disorder due to the size distribution of nanocrystals. Both are represented by normal distributions of width $\sigma_L$ and $\sigma_N$ respectively, which have the effect of smoothing the superlattice fringes (Figure 2c-d). The multilayer diffraction
method retrieves the values of those five parameters \((d, N, L, \sigma_L, \sigma_N)\) through a least square minimization. As an example, the values of structural parameters for the fit shown in Figure 2d are listed within panels a-d.

![Figure 2. Structural parameters in the multilayer diffraction method.](image)

The superlattice fringes decorating the diffraction profile are especially sensitive to \(\sigma_L\). If this parameter becomes too large, the fringes fade, and the peak shape becomes that of the unmodulated nanocrystal form factor. The sensitivity of superlattice fringes to \(\sigma_L\) gets higher with the fringe index, which explains the almost complete lack of modulation at the second Bragg peak. This can be exploited for a quick estimate of the average nanocrystal stacking displacement \(\delta_N\) by simply observing whether a certain Bragg peak contains fringes or not:

\[
\delta_N \leq \frac{\pi}{2q} \quad \text{(Eq. 1)}
\]

where \(q\) indicates the Bragg peak position (for derivation of Eq. 1 see SI, section S.k). Since for CsPbBr\(_3\) superlattices the first Bragg peak shows fringes, while the second does not, Eq. 1 estimates that the average stacking displacement is \(0.7 \text{ Å} < \delta_N < 1.4 \text{ Å}\). Notably, \(\delta_N\) has the same magnitude of \(\sigma_N\), as both are a few percent of \(\Lambda\) and much smaller than a CsPbBr\(_3\) perovskite unit cell \((d \approx 5.8 \text{ Å})\), which points to a remarkable structural order.
Comparison of the multilayer diffraction method with established techniques. Since the multilayer diffraction method is new to colloidal superlattices, we performed a validation by comparing the fit results on the room-temperature θ:2θ pattern of CsPbBr₃ superlattices, found in Table 1, with those from GISAXS, GIWAXS and SAED analyses on a replica sample (Figure 3, see SI section S.I for a detailed discussion). The GISAXS determined a simple-cubic superlattice symmetry with \( \Lambda = 103 \pm 1 \) Å, which is in a good agreement with the periodicity obtained by the multilayer diffraction method (\( \Lambda = 106.95 \) Å, within synthesis variability). GIWAXS and SAED qualitatively confirmed the high structural order of the superlattices, also consistent with results of Eq.1. To compare, the θ:2θ XRD is a one-dimensional measurement constrained to the direction perpendicular to the substrate, thus the multilayer diffraction method cannot determine the packing symmetry. On the other hand, it allows the simple quantification of \( \sigma_L \) and the separation of \( \Lambda \) into its \( N \), \( d \) and \( L \) contributions. All these parameters can be in principle measured by GISAXS and GIWAXS, but that would require a resource-intensive effort due to complexity of two-dimensional data, which is arguably the reason why examples in the literature are rare.⁸,¹⁰

![Figure 3. Comparison of the multilayer diffraction method with established techniques.](image)

**Figure 3.** Comparison of the multilayer diffraction method with established techniques. a) Representation of the diffraction geometries adopted for experiments in panels b-d, highlighting the complementarity of grazing incidence techniques and TEM-SAED in terms of probed spatial directions. b) GISAXS pattern of CsPbBr₃ superlattices indexed according to a simple-cubic symmetry. The diffraction spots are generated by the nm-scale periodicity of the mesostructure. c) GIWAXS pattern of CsPbBr₃ superlattices. The spots arise from the Å-scale periodicity of the CsPbBr₃ nanocrystal atomic lattice. d) SAED pattern of a single CsPbBr₃ superlattice, featuring slightly elongated spots again produced by the atomic lattice. The beam-stopper was masked for illustration purposes. Data in panels c and d were indexed using a pseudo-cubic notation for simplicity.
A case-study: thermal annealing of CsPbBr₃ superlattices. The high sensitivity of the multilayer diffraction method to small changes in the superlattices structural parameters makes it an excellent tool for tracking the superlattice evolution under external stimuli. This is demonstrated by analyzing a set of 6:29 XRD patterns collected during the thermal annealing of CsPbBr₃ superlattices in the 25-125°C temperature range (above this temperature, nanocrystals start to coalesce leading to the irreversible degradation of superlattices, Figure S8). As the temperature rose from 25 °C, all the three regions of the diffraction pattern evolved, as exemplified by the changes in the first Bragg peak profile (Figure 4a, see Section S.m for the evolution of low-angle and second Bragg peak regions).

Focusing on the first Bragg peak, the multilayer diffraction model correctly follows the anticipated thermal expansion of the CsPbBr₃ atomic lattice (d=5.838→5.872 Å, Figure 4b). The measured value for d is consistent with expectation, remaining in between the lattice constants reported for orthorhombic and tetragonal CsPbBr₃. The parameter evolution with temperature better matches that reported for the shorter orthorhombic axes, suggesting that nanocrystals might be preferentially oriented with their long axis c parallel to the substrate. The change of slope likely corresponds to the orthorhombic → tetragonal → cubic transition, taking place at a lower temperature than reported for bulk in agreement with reports in the literature. Despite the nanocrystal lattice expansion, Λ contracts due to the shrinking of the interparticle spacing (L=36.9→35.1 Å, Figure 4c). The superlattice contraction is similar to that previously reported under vacuum, partly due to the desorption of volatile molecules trapped in between the nanocrystals (e.g. solvent). However, the superlattices in this work have been kept under vacuum prior to the thermal annealing, suggesting that the melting of surface capping molecules (i.e. oleylammonium bromide and cesium oleate, which are solid at room temperature) may also contribute to the mesostructure contraction via the interdigitation of hydrocarbon tails.

The thermal annealing of superlattices leads to a significant reduction of the nanocrystal stacking disorder (σₐ₁=1.43→1.01 Å, Figure 4d) which is rationalized as an increase in the superlattice crystallinity: entrapped molecules and misplaced ligands represent crystallographic defects of the mesostructure, and their removal by thermal annealing improves the structural order. Additionally, the CsPbBr₃ orthorhombic → tetragonal → cubic phase transition is likely contributing to the reduction of disorder, due to the progressively increasing symmetry of the nanocrystal structure. We highlight that σₐ remained constant between 100°C and 125°C, suggesting that the maximum structural order achievable by annealing was reached. Besides these three main parameters, the extracted nanocrystal thickness and thickness distribution remained constant at N = 13 atomic planes (Figure S9) and σₐ ≈ 1.36 (in units of atomic planes, Figure S9), with fluctuations within the fit uncertainty.
CsPbBr$_3$ nanoplatelet stacks. The multilayer diffraction method has its roots in epitaxial multilayer thin films; thus, it naturally applies to the closest colloidal analogues, namely stacks of self-assembled nanoplatelets. The first example are CsPbBr$_3$ nanoplatelets, which are colloidal quantum wells widely studied for applications in solution-processed blue LEDs. Here we analyzed the $\theta$:2$\theta$ XRD pattern of CsPbBr$_3$ nanoplatelets prepared by a recently optimized robotic synthesis. The nominal thickness of the CsPbBr$_3$ nanoplatelets was reported to be 2 monolayers on the basis of optical measurements and electron microscopy (1 monolayer = a single plane of [PbBr$_6$]$^{4-}$ octahedra).

Figure 5 compares the second Bragg peaks of CsPbBr$_3$ nanoplatelet and nanocrystal superlattices over the same q-range; the best fit parameters are summarized in Table 1. The comparison demonstrates the applicability of our fit to higher-order Bragg peaks and highlights the differences between the two samples. The CsPbBr$_3$ nanoplatelets thinness results in a very broad form factor, which allows the observation of multiple superlattice fringes. The expected thickness of two [PbBr$_6$]$^{4-}$ octahedra layers is consistent with the measured 4 diffracting planes with a periodicity of ≈3 Å, compatible with the length of one Pb-Br bond. The value $\sigma_L$ =0.68 Å is remarkably small and fulfills the $\delta_L$ criterion (Eq.1). The smaller stacking disorder explains why superlattice fringes are visible for the nanoplatelets but not for the nanocrystals, for which $\sigma_L$ is more than doubled. Remarkably, $d$ differs significantly between nanocrystals and nanoplatelets (5.838 vs 6.038 Å), corresponding to a 3.4% atomic lattice expansion.
along the stacking direction for nanoplatelets as compared to nanocrystals (see SI, section S.o). This size-dependent relaxation effect is consistent with prior studies on colloidal quantum dots, e.g. PbSe, and has been previously measured in six monolayer-thick CsPbBr₃ nanoplatelets by means of pair distribution function analysis.

Figure 5. CsPbBr₃ nanoplatelets stacks. a) The second Bragg peak of CsPbBr₃ nanoplatelets stacks [N=4 for pseudocubic plane (200), meaning N=2 for plane (100)] compared with b) the second Bragg peak of CsPbBr₃ nanocrystal superlattices (N = 13 for plane (100)). The comparison demonstrates the much broader modulation profile in the case of nanoplatelets, due to their extreme thinness, and the large number of fringes due to the higher structural perfection of nanoplatelets stacks as compared to nanocrystals (σ_L = 0.682 Å vs 1.43 Å, respectively). The sketches of the superlattices of nanoplatelets and nanocrystals are shown on the right, with the best fit values of their structural parameters.

PbS nanoplatelet and nanocrystal superlattices. The multilayer diffraction effect is very apparent in lead halide perovskite superlattices, but is not limited to that class of materials. This is demonstrated on assemblies of recently synthesized ultrathin PbS orthorhombic nanoplatelets (Figure 6a-d) and spheroidal rock-salt PbS nanocrystals (Figure 6e-g). For both the morphologies, particles assemble with the same crystal planes parallel to the substrate [cubic (200) = orthorhombic (400)], a circumstance convenient for the comparison. Table 1 summarizes the result of the fits. As for CsPbBr₃, stacks of PbS nanoplatelets produce a broad group of superlattice fringes (Figure 6a), which extend away from the strongest peak to low angles thanks to the side bands of the nanosheet form factor (Figure 6b). The large number of observed fringes allows the fit-independent determination of Λ = 53.45 Å (Figure 6c) by exploiting the periodicity of fringes along the q-scale (q_n = 2πn/Λ, where n is a fringe index), a result in agreement with that from the multilayer diffraction fit. The best fit parameters N, d and Λ are in a good agreement with previously reported literature values obtained by independent methods (from ref.: d = 2.978 Å; N = 4 Pb-S planes, Λ = 54 Å). Remarkably, the PbS nanoplatelets displacement value of σ_L ≈ 0.32 Å is the smallest disorder measured among the four studied superlattices.

In contrast with the other samples, assemblies formed by spheroidal PbS nanocrystals showed no superlattice-related Bragg peak fine structure (Figure 6e) despite the well-defined microscopic superlattice shapes (Figure 6g) and the strong preferred orientation of nanocrystals witnessed by the sole (002) Bragg peak (Figure 6f).
of superlattice fringes is explained by a rotational disorder due to the rounded shape of nanocrystals (inset in Figure 6g), which brings the PbS nanocrystal superlattices beyond the maximum disorder threshold of $\delta \Lambda < 0.7$ Å (from Eq. 1; further discussion in SI, section S.p). Therefore, only the nanocrystal form factor is visible, from which the multilayer diffraction method enables the precise determination of the average nanocrystal thickness in the vertical direction ($N = 32 \rightarrow 92.3$ Å).

Figure 6. PbS nanoplatelet and nanocrystal superlattices. a) Fit of the (400) orthorhombic = (200) pseudocubic Bragg peak of PbS nanoplatelet stacks. b) The full pattern acquired from PbS nanoplatelet stacks, showing superlattice fringes extending to lower angles. c) Plot demonstrating the linear distribution of the superlattice fringes in $q$-space. d) A representative TEM image of PbS ultrathin nanoplatelets. e) Fit of the PbS nanocrystal superlattices (200) Bragg peak. f) The full pattern acquired from PbS nanocrystal superlattices, showing no fringes but clearly indicating the strong preferred orientation of nanoparticles. g) A representative optical microscopy image of the PbS nanocrystal superlattices together with a representative TEM image of PbS nanocrystals (inset). The nanocrystal diameter measured by TEM is $11.5 \pm 1.0$ nm, while the thickness measured by multilayer diffraction is 9.2 nm, suggesting that nanoparticles have the shape of a compressed sphere, that also explains the complete preferred orientation seen in 6:29 XRD.
Table 1. Best fit structural parameters of the nanocrystal superlattices at room temperature.

| Sample                  | $d$ (Å)       | $L$ (Å)       | $\sigma_L$ (Å) | $N$ (planes) | $\sigma_N$ (planes) | $\Lambda$ (Å) |
|------------------------|---------------|---------------|----------------|--------------|---------------------|---------------|
| CsPbBr$_3$ Nanocrystals | 5.8376 ± 0.0019† | 36.899 ± 0.037 | 1.428 ± 0.015 | 12.92 ± 0.10  | 1.55 ± 0.32         | 106.950 ± 0.043 |
|                         |               |               |                | (75.9 Å thick)§ |                    |               |
| CsPbBr$_3$ Nanoplatelets | 3.0343 ± 0.0021 (2° B. peak) | 33.529 ± 0.014 | 0.682 ± 0.001 | 3.954 ≈ 4     | 0.31 ± 0.017       | 42.632 ± 0.015 |
| PbS Nanosheets          | 3.0233 ± 0.0042 | 44.3933 ± 0.029 | 0.3236 ± 0.0158 | 3.9825 ± 0.0505 | 0.817 ± 0.078 | 53.463 ± 0.032 |
| PbS Nanocrystals        | 2.9781 ± 0.0007 | n/a           | > 1.5‡ (δ$\Lambda$ > 0.7) | 31.85 ≈ 32 ± 0.78 | 5.3 ± 1.5 | n/a |

†Error bars were evaluated via bootstrap analysis (see SI, section S.j) and error propagation (for $\Lambda$).
‡For PbS nanocrystal superlattices, $\sigma_\Lambda$ was estimated based on the relative $\chi^2$ map (Figure S11).
§The nanocrystal thickness is defined in the section S.d of the SI.

Discussion and perspectives. The examples above introduce the multilayer diffraction method as a powerful tool for the detailed characterization of both the nanocrystals and the superlattices they form. Here, we discuss ideal conditions for its applications, and outline its limitations. Data analysis via multilayer diffraction method is suitable for well-ordered superlattices composed of nanocrystals with restricted rotational freedom. Well-faceted or strongly anisotropic particles, such as cubes or platelets, are ideal. Otherwise, as seen for PbS spheroidal nanocrystals, the method is limited to the analysis of the nanocrystal shape factor. The atomic lattice of nanocrystals is important too: materials with low-angle peaks ($2\theta < 20^\circ$) benefit from the higher tolerance of lower-index fringes to the superlattice structural disorder. That is the reason why the multilayer diffraction model is ideal for lead-halide perovskites, where the combination of the broader form factor and better stacking extend the working range above 30°.

Focusing on its practical utility, the multilayer diffraction method provides new insights on colloidal superlattices. First, the annealing of CsPbBr$_3$ nanocrystal superlattices results in their contraction and an improved structural order. This is likely due to the combination of factors such as ligand interdigitation, loss of impurities, and increased nanocrystal lattice symmetry at higher temperatures. Other factors might coexist, like the intriguing possibility of superlattice defects annihilation (e.g. crowdions-voidions pair). Second, the sensitivity to the atomic planes periodicity $d$ revealed an anisotropic 3.4% expansion of the CsPbBr$_3$ structure in going from N=13 nanocubes to N=2 in nanoplatelets, indicating that the approximate $d = 5.8$ Å value often used to estimate the thickness of a single [PbBr$_6$]$^2-$ octahedron is imprecise for thin nanostructures. Third, the superlattice periodicity fluctuation ($\sigma_L$) establishes a figure of merit for the superlattice structural perfection and its upper boundary can be quickly estimated from the Eq. 1. The obtained values of $\sigma_L$ are much smaller than the atomic planes periodicity of the inorganic material forming the superlattice (~3 Å for both CsPbBr$_3$ and PbS). Surprising at first, this result is comparable to the periodicity fluctuations measured in epitaxial multilayer thin films grown by physical means (e.g. $\sigma_\Lambda$<1.4 Å for Pb / amorphous Ge and $\sigma_\Lambda$≈0.5 Å for MgPt$_3$/Co multilayers). The $\sigma_L$ values of 0.3-1.4 Å determined in this work are comparable to the atomic displacement parameters found in some metalorganic crystals.
(e.g. B=0.38 Å in silver behenate, a small-angle scattering standard)\(^4\) and roughly an order of magnitude smaller than the displacements reported for other colloidal nanocrystal superlattices (e.g. 0.5-0.9 nm in Fe\(_3\)O\(_4\) and 1.15 nm in FePt nanocrystal superlattices, both by GISAXS).\(^8\),\(^10\) This remarkable structural order poses a fundamental question: can colloidal superlattices be considered as microscopic single crystals? For example, the CsPbBr\(_3\) nanocrystal superlattices in this study can be seen as “zero-dimensional” equivalents of hybrid organic-inorganic layered metal-halides.\(^4\) This interpretation should be taken with a grain of salt, as it is based on the order characterized along a single spatial dimension.

The information made accessible by the multilayer diffraction method, and the resulting change of perspective about colloidal superlattices, might open new routes in the research on similar materials. Assemblies of other widely-studied nanocrystals, such as colloidal CdE (E= S, Se, Te) nanoplatelets,\(^42\),\(^43\) will likely benefit from the developed approach. CdE nanoplatelets show reflections at relatively low-angles (2θ ~25-26°, q~1.8 Å\(^{-1}\)), which combined with their precise thickness are anticipated to produce superlattice fringes. It might be suitable for higher-complexity nanomaterials too, e.g. to investigate the role of epitaxial interface in stacks of digital or core-crown II-VI heterostructured nanoplatelets,\(^44\) or explore individual sublattices in binary superlattices\(^12\) by exploiting the material-dependent scattering angle. On the other hand, the multilayer diffraction method could also be extended to hybrid organic-inorganic 2D layered materials.\(^4\) Although within the reach of single-crystal X-ray diffraction, those materials could benefit from a simpler analysis via 0:2θ XRD scans coupled with a multiparametric fit.

**CONCLUSIONS**

The multilayer diffraction method enabled us to demonstrate that colloidal superlattices can approach the structural perfection of single crystals. In principle, this means that a wide range of techniques usually applied to single crystals might be now accessible for the characterization of individual nanocrystals, exploiting superlattices as a tool. One natural parallel arising from diffraction is with protein crystallography, that studies complex nanometric structures by probing their aggregates, but the same goes for the investigation of any anisotropic property. For example, one can think of anisotropic magnetic measurements, polarized spectroscopies, and even direct mapping of the electronic structure.\(^45\) We really believe that exploiting superlattices as a tool will advance research on colloidal nanocrystals, and we hope that the findings we hereby presented will further encourage research in that direction.
MATERIALS AND METHODS

Chemicals. Lead bromide (PbBr$_2$, $\geq$98%), lead thiocyanate (Pb(SCN)$_2$, 99.5%), cesium carbonate (Cs$_2$CO$_3$, 99%) oleylamine (OLAM, 70%), oleic acid (OA, 90%), 1-octadecene (ODE, 90%), tetrachloroethylene, toluene (TOL, anhydrous, 99.8%), Lead(II) acetate trihydrate (≥99.5%), benzoyl bromide (97%) and dodecane were purchased from Sigma-Aldrich. Cesium acetate (99%) and ethyl acetate (≥99.5%) were purchased from Fisher Scientific. All chemicals were used without further purification; lead compounds were stored in inert N$_2$ atmosphere.

Synthesis of CsPbBr$_3$ nanocrystal superlattices. CsPbBr$_3$ nanocrystal superlattices were grown following our previously published method from tetrachloroethylene or toluene dispersions of CsPbBr$_3$ nanocrystals. To synthetize the starting CsPbBr$_3$ nanocrystals, 74 mg (0.2 mmol) of PbBr$_2$ were dissolved in 5 ml of ODE together with 500 μL of OLAM and 50 μL of OA at 120° under N$_2$ atmosphere, continuous stirring and inside a 20 mL glass vial. After the solubilization was completed, the vial was heated up to 170°C, removed from the hotplate and let cool in air down to the desired injection temperature (usually 163°C). Then, 0.5 mL of a previously prepared solution of Cs-oleate in ODE (0.149 M) were swiftly injected, and the system was let cooling down to room temperature in air. CsPbBr$_3$ nanocrystals were recovered by centrifugation at 6000 rpm for 5 minutes. The supernatant was discarded, and the precipitate was centrifuged again to separate the traces of residual supernatant. The collected liquid was removed with a paper tissue, the precipitate was redispersed in a small volume of solvent (≈ 200 μL) and centrifuged again at 6000 rpm for 5 minutes to separate aggregates and larger particles. The resulting concentrated CsPbBr$_3$ nanocrystal dispersion was diluted with a solvent until an extrapolated optical density of ≈250 at 335 nm and 10 mm pathlength to form a stock solution for self-assembly. A small amount of stock solution, typically 30 μL, was deposited on top of a 1 x 1 cm polished piece of silicon wafer and placed inside a glass Petri dish to let the solvent evaporate overnight.

Synthesis of CsPbBr$_3$ nanoplatelets superlattices. Lead and cesium oleate solutions were prepared in line with previous descriptions by Lu et al. 192 mg (1 mmol) of cesium acetate were placed into a 4 mL glass vial with stir bar, and 1 mL of OA was added. For lead oleate solutions, 379 mg (1 mmol) lead acetate were placed into a 4 mL glass vial with stir bar, and 1.5 mL of OA was added. The mixtures were stirred for 3 hours at 100 °C on a hot plate and used without further purification, except for brief reheating before synthesis to ensure full mixing of precursors. The sample of 2-monolayer thick CsPbBr$_3$ nanoplatelets was prepared as reported previously in a method derived from the synthesis scheme reported by Imran et al. Dodecane (1 mL), 60 μL OLAM, 80 μL OA, 10 μL (0.1 mmol Cs) cesium oleate solution (1 M), 30 μL (0.2 mmol Pb) lead oleate solution (0.67 M) were added to a 4 mL glass vial equipped with a stir bar and heated to 100 °C. 10 μL of benzoyl bromide were then injected to the solution while stirring to start the reaction. After 1 minute, 1 mL ethyl acetate was added to form a cloudy suspension. Solid products were collected by centrifugation (10 g, 2 min) and resuspended in 1 mL hexanes. To create superlattices for XRD measurement, 100 μL of 2-monolayer nanoplatelet solution in hexanes was drop-cast on a Si wafer (5 cm radius, <510> cut) and evaporated under a nitrogen stream.

Synthesis of PbS nanoplatelet and nanocrystal superlattices. PbS nanoplatelet stacks were prepared following our previously published method. Briefly, 32 mg (0.1 mmol) of Pb(SCN)$_2$ were dissolved in 5 mL of ODE together with 125 μL of OLAM and 250 μL of OA at 120° under N$_2$ atmosphere, continuous stirring and inside a 25 mL three necked flask. After the solubilization was completed, the vial was quickly heated up to 150-180 °C. The fast heating triggered the nanoplatelet formation that manifested itself by the sudden change in the color of the reaction mixture from pale yellow to black. The reaction was quenched as soon as the color change was complete.
by immersion in a mixture of water and ice. PbS nanoplatelet were recovered by centrifugation at 6000 rpm for 5 minutes. The supernatant was discarded, and the precipitate was centrifuged again to remove the residual supernatant. The precipitate was then redispersed in a small volume of toluene (≈ 500 μL). PbS nanoplatelets stacks were obtained by drop-casting a small amount of toluene solution of freshly prepared nanoplatelets on a zero-diffraction silicon wafer and letting it dry in air.

PbS nanocrystals were grown via a modification of the method we originally published for the synthesis of lead chalcohalide nanocrystals. Briefly, 111 mg (0.4 mmol) of PbCl2 were dissolved in a 20 mL flask containing 10 mL ODE, 750 μL OLAM and 750 μL OA at 120°C under continuous stirring. The solubilization of PbCl2 is slow and might be incomplete. To remove any undissolved precursor, the reaction mixture was cooled down to room temperature after 20 minutes of stirring at elevated temperature and filtered through a 0.2 μm PTFE filter (Sartorius®). Afterwards, the filtered reaction mixture was placed back into the flask and heated up to 170°C, the formation of nanocrystal was accompanied by the color change of the reaction mixture from pale yellow to black, at which point the reaction was quenched by submerging the flask in a room temperature water bath. The PbS nanocrystals were separated from the reaction mixture following the procedure described above for CsPbBr3 nanocrystals. After that, one synthetic batch was diluted in 400 μl of toluene, split in 4 aliquots and further diluted at 1:1, 1:2, 1:3 and 1:4 ratios to quickly scan many possible assembly concentrations. A small amount of each solution, typically 30 μL, was deposited on a 1 x 1 cm silicon substrate, and the four substrates were enclosed in a single non-sealed Petri dish to dry overnight. All the samples formed superlattices, demonstrating the high attitude of those nanocrystals to self-assemble.

Thermal annealing of CsPbBr3 nanocrystal superlattices. Prior to the annealing experiments, a sample of CsPbBr3 nanocrystal superlattices (1 x 1 cm piece of silicon wafer with the superlattices on top) was placed under vacuum for 2h to complete the drying. After that, it was mounted in a controlled-atmosphere heating stage filled with N2 and covered within a Kapton dome transparent to X-rays. The XRD patterns were acquired every 25°C, starting from room temperature (≈25°C) and up to 300°C. The sample was heated at a speed of 10°C/min with a thermalization time of 10 min before each measurement. A measurement at each temperature set point took ~10 minutes.

θ:2θ coupled out-of-plane diffraction of superlattices. θ:2θ coupled X-ray diffraction (θ:2θ XRD) patterns of superlattices were acquired alternatively on three different diffractometers. 1) Panalytical Empyrean diffractometer, equipped with a 1.8 kW CuKα ceramic X-ray tube operating at 45 kV, 1 mm wide incident and receiving slits, and 40 mA and a PIXcel3D 2x2 area detector, parallel-beam geometry. 2) Rigaku SmartLab diffractometer, equipped with a 9kW CuKα rotating anode operating at 40 kV and 150 mA, 1 mm wide incident and receiving slits, and 0D scintillation counter (SC) detector, parallel-beam geometry. 3) Bruker D2 Phaser X-ray diffractometer equipped with a 30 kV Cu Kα operating at 10 mA, 1 mm wide incident slits, 1 cm knife edge with parallel beam geometry and SSD160 silicon strip detector.

GISAXS and GIWAXS measurements. GISAXS and GIWAXS measurements. GISAXS and GIWAXS measurements were performed on a Rigaku instrument equipped with a Fr-E+ superbright rotating anode microsource (CuKα, λ=1.5405 Å) coupled to a three pinhole camera through a Confocal Max Flux optics. A Triton multiwire detector with online readout was used to collect GISAXS data, at a sample-to-detector distance (SDD) of 2110 mm. An image plate detector with offline readout (RAXIA) was used to collect GIWAXS data, at a
SDD of 87 mm. Both GISAXS and GIWAXS were acquired both at room pressure and in vacuum (≈ 5 x 10^{-2} mbar) to keep track of the vacuum-induced superlattice contraction effect we reported in our previous work.\textsuperscript{21} Data were calibrated by using Ag Behenate standard powder. GISAXS patterns were acquired at three different grazing incidence angles (GA = 0.18° – 0.28° – 0.38°) to provide a robust dataset, while GIWAXS patterns were acquired at 0.28° and 2° incidence. The data analysis was performed on the patterns acquired at GA = 0.28° in vacuum, as this combination provided the lowest background scattering and better visibility of GIWAXS in-plane reflections. GISAXS data analysis was performed by using the SUNBIM software suite.\textsuperscript{49} Indexing was performed based on the Nanocell algorithm included in Sunbim.\textsuperscript{50} Superlattice periodicity (Λ) was derived both: i) by extracting linear cuts through the main diffraction spots spaced by Δq and calculating Λ=2π/Δq; ii) by direct simulation of the 2D diffraction pattern through the indexing program, and visually identifying the lattice parameters leading to the best agreement with the experimental pattern, within an acceptable tolerance. The average from the two procedures was taken as the final result. GIWAXS data analysis was performed combining both SUNBIM (data calibration) and the GIXSGUI software suite (indexing).\textsuperscript{51}

**TEM, HR-SEM and optical microscopy.** Transmission electron microscopy (TEM) images of nanocrystals were acquired on a JEOL JEM-1011 microscope equipped with a thermionic gun at an accelerating voltage of 100 kV and on a JEOL JEM-1400Plus microscope working at 120 kV. Selected Area Electron Diffraction (SAED) patterns were acquired on a JEOL JEM-1400Plus microscope. The samples were prepared by depositing 3 μL of a diluted nanocrystal suspension in TCE onto 200 mesh carbon-coated copper grids, and letting it dry slowly. The indexing of SAED data was performed with the help of CaRIne Crystallography software suite, via a simulation of the reciprocal atomic lattice. High resolution scanning electron microscopy (HR-SEM) images were acquired on a JEOL JSM-7500FA SEM microscope. Optical images were acquired on a Zeta-20 optical confocal profilometer.

**Using the Multilayer Diffraction fitting algorithm.** The Multilayer Diffraction fitting algorithm presented in this work is provided in the form of an open-source Python code optimized for running in the Jupyter environment. Individual Jupyter notebooks and experimental input data for the four types of nanocrystal superlattices discussed in this work (CsPbBr\textsubscript{3} nanocrystals and temperature series, CsPbBr\textsubscript{3} nanoplatelets, PbS nanoplatelets, PbS nanocrystals) are provided in a *.zip archive as a part of the SI.

Raw data requires some preparation for the fit. The output format of diffractometers is usually 2θ(°)/Intensity, which must be converted into \( q(\text{Å}^{-1})/\text{Intensity} \) according to the equation \( q = 4\pi \cdot \sin(\theta)/\lambda_{\text{x-ray}} \). Input must be prepared in the form of a double-column comma separated .csv spreadsheet, containing the scattering vector in the first column and the diffracted intensity in the second. If the signal to background ratio is high the raw experimental data could be fit (as in Figure 4), otherwise a background subtraction is needed. For example, in the case of Figure 5a and Figure 6a the instrumental background was not negligible, thus it was described by a spline with the guidance of the residual curve and subtracted. In addition, the pattern in Figure 5a contained peaks not belonging to the superlattices, which were fitted with a gaussian profile and subtracted (Figure S10). The so-prepared pattern is fed to the Multilayer Diffraction fitting algorithm, together with starting values and fitting boundaries for each parameter. The superlattice structural parameters \( (d, L, σ_L, S, σ_S) \) are defined in Figure 2 and Table S1. In addition to these, the model relies on four instrumental parameters: q-zero correction, instrumental broadening parameter, coherence length and experimental intensity fluctuation. Additional details are provided in Table S1 and sections S.b-g of the SI.
We suggest exploiting the simulation functionality of our program, which predicts the pattern with given parameters, to check if their starting values are meaningful. Most can be guessed based on the prior knowledge about the sample: \( d \) is known from the nanoparticle crystal structure, \( N \) and \( \Lambda \) can be estimated from TEM, while \( L \) depends on the choice of passivating ligands (20-50 Å range for oleylamine and oleic acid). The \( \sigma_L \) value can be conveniently changed from very high (e.g. \( = 10 \)) to eliminate the superlattice interference while checking \( d \) and \( N \), to very low (e.g. \( = 0.1 \)) to sharpen the superlattice fringes while checking \( L \) and \( N \). Finally, \( \sigma_S \) is better set to low values at first (e.g. \( = 0.1 \)). Regarding instrumental parameters, \( C \) should start at a high value (e.g. \( = 20 \)), while the q-zero correction should be initially set to \( 0 \) Å\(^{-1} \). The instrumental broadening and experimental intensity fluctuation are the constants to be measured a priori as illustrated in sections S.b and S.i of the SI. Once starting values and boundaries have been set, the program relies on least square minimization to find the best fit for the experimental profile. The program let the user define up to three regions of interest, which enter the fit with adjustable weights. It is advisable to limit each region to a restricted range, e.g. one single Bragg peak or one single fringe, because the program in its current state does not include the q-dependent intensity corrections needed for fitting over wide ranges. This is particularly useful to fit the q-zero correction (see SI, section S.g).

Once satisfactory starting values are found, the algorithm refines their values by fitting the experimental profile. Once the fit is concluded, the program allows the user to explore the influence of individual parameters on the goodness of fit by plotting the \( \chi^2 / \) parameters maps and estimates the error bars via a bootstrap approach, which requires the user to estimate the fluctuation of the diffracted intensity measured experimentally. We did this by repeating three identical scans over one sample, finding that the average fluctuation was 3%. The program uses this value to introduce a random error in multiple replicas of the experimental data, which are then fit and used to compute the average value and standard deviation of parameters.

**ASSOCIATED CONTENT**

**Supporting Information.** The Supporting Information is available free of charge on the ACS Publications website at DOI:

- Discussion of superlattice reflections in the low angle region, a complete description of the multilayer diffraction model and its implementation, discussion of the physical meaning of \( L \), \( N \), \( \sigma_N \) parameters and coherence length, application of q-zero correction to the input data, \( \chi^2 \) maps for CsPbBr\(_3\) superlattices, evaluation of experimental X-ray scattering intensity fluctuation, description of the bootstrapping algorithm, derivation and application of Equation 1, additional discussion of GISAXS, GIWAXS, and SAED results, XRD patterns of thermal annealing series of CsPbBr\(_3\) nanocrystal superlattices, evolution of fitted \( N \) and \( \sigma_N \) parameters during annealing, treatment of XRD data of CsPbBr\(_3\) nanoplatelet superlattices, \( \chi^2 \) maps for and rotational disorder in PbS nanocrystal superlattices, additional references. (PDF)
- Experimental XRD data for CsPbBr\(_3\) nanocrystal and nanoplatelet superlattices (including thermal annealing series), PbS nanocrystal and nanosheets superlattices, and individual Jupyter Notebooks with the fitting routines for each data. (ZIP)
AUTHOR INFORMATION

Corresponding Authors

*E-mail: dmitry.baranov@iit.it
*E-mail: cinzia.giannini@ic.cnr.it
*E-mail: liberato.manna@iit.it

Notes

The authors declare no competing financial interest

Author Contributions

S.T. and D.B. contributed equally.

ACKNOWLEDGEMENTS

The work of D. Baranov was supported by the European Union’s Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No. 794560 (RETAIN). The visit of S. Toso to Cornell University was supported by the European Union’s Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No. 691185 (COMPASS). Work on perovskite nanoplatelets was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Materials Sciences and Engineering Division, under Contract No. DEAC02-05-CH11231 within the Physical Chemistry of Inorganic Nanostructures Program (KC3103). J.C. Dahl acknowledges support by the National Science Foundation Graduate Research Fellowship under DGE 1752814 and by the Kavli NanoScience Institute, University of California, Berkeley through the Philomathia Graduate Student Fellowship. The C.Giannini, D. Altamura, and F. Scattarella (IC-CNR) acknowledge support from the PON "R&I"2014- 2020 “Energie per l’Ambiente TARANTO - Tecnologie e processi per l'Abbattimento di inquinanti e la bonifica di siti contaminati con Recupero di mAterie prime e produzioNe di energia TOtally green"- Code: ARS01_00637 (CUP: B86C18000870005). We thank R. Lassandro for the technical support in the XMI-Lab, Dr. B. Martín-Garcia, Dr. Q. A. Akkerman, Dr. O. Gorobtsov and Mr. W. Qiu for technical assistance and helpful discussions, Dr. R. Brescia and Mr. S. Lauciello (Electron Microscopy Facility at IIT) for help with electron microscopy analysis of superlattices.
REFERENCES

(1) Giannini, C.; Holy, V.; De Caro, L.; Mino, L.; Lamberti, C. Watching Nanomaterials with X-Ray Eyes: Probing Different Length Scales by Combining Scattering with Spectroscopy. *Prog. Mater. Sci.* **2020**, *100667*. https://doi.org/10.1016/j.pmatsci.2020.100667.

(2) Holder, C. F.; Schaak, R. E. Tutorial on Powder X-Ray Diffraction for Characterizing Nanoscale Materials. *ACS Nano* **2019**, pp 7359–7365. https://doi.org/10.1021/acsnano.9b05157.

(3) Li, T.; Senesi, A. J.; Lee, B. Small Angle X-Ray Scattering for Nanoparticle Research. *Chemical Reviews* **2016**, pp 11128–11180. https://doi.org/10.1021/acs.chemrev.5b00690.

(4) Weidman, M. C.; Seitz, M.; Stranks, S. D.; Tisdale, W. A. Highly Tunable Colloidal Perovskite Nanoplatelets through Variable Cation, Metal, and Halide Composition. *ACS Nano* **2016**, *10*(8), 7830–7839. https://doi.org/10.1021/acsnano.6b03496.

(5) Corricelli, M.; Altamura, D.; Curri, M. L.; Sibillano, T.; Siliqi, D.; Mazzone, A.; Depalo, N.; Fanizza, E.; Zanchet, D.; Giannini, C.; Striccoli, M. GISAXS and GIWAXS Study on Self-Assembling Processes of Nanoparticle Based Superlattices. *CrystEngComm* **2014**, *16*(40), 9482–9492. https://doi.org/10.1039/c4ce01291g.

(6) Altamura, D.; Sibillano, T.; Siliqi, D.; De Caro, L.; Giannini, C. Assembled Nanostructured Architectures Studied by Grazing Incidence X-Ray Scattering. *Nanomater. Nanotechnol.* **2012**, *2*(1), 2–16. https://doi.org/10.5772/55777.

(7) Vegso, K.; Siffalovic, P.; Benkovicova, M.; Jergel, M.; Luby, S.; Majkova, E.; Capek, I.; Kocsis, T.; Perlich, J.; Roth, S. V. GISAXS Analysis of 3D Nanoparticle Assemblies Effect of Vertical Nanoparticle Ordering. *Nanotechnology* **2012**, *23*(4). https://doi.org/10.1088/0957-4484/23/4/045704.

(8) Heitsch, A. T.; Patel, R. N.; Goodfellow, B. W.; Smilgies, D. M.; Korgel, B. A. GISAXS Characterization of Order in Hexagonal Monolayers of FePt Nanocrystals. *J. Phys. Chem. C* **2010**, *114*(34), 14427–14432. https://doi.org/10.1021/jp1047979.

(9) Boles, M. A.; Engel, M.; Talapin, D. V. Self-Assembly of Colloidal Nanocrystals: From Intricate Structures to Functional Materials. *Chem. Rev.* **2016**, *116*(18), 11220–11289. https://doi.org/10.1021/acs.chemrev.6b00196.

(10) Altamura, D.; Holý, V.; Siliqi, D.; Lekshmi, I. C.; Nobile, C.; Maruccio, G.; Cozzoli, P. D.; Fan, L.; Gozzo, F.; Giannini, C. Exploiting GISAXS for the Study of a 3D Ordered Superlattice of Self-Assembled Colloidal Iron Oxide Nanocrystals. *Cryst. Growth Des.* **2012**, *12*(11), 5505–5512. https://doi.org/10.1021/cg3010739.

(11) Florea, I.; Demortière, A.; Petit, C.; Bulou, H.; Hirlimann, C.; Ersen, O. 3D Quantitative Analysis of Platinum Nanocrystal Superlattices by Electron Tomography. *ACS Nano* **2012**, *6*(3), 2574–2581. https://doi.org/10.1021/nn205029s.

(12) Friedrich, H.; Gommes, C. J.; Overgaag, K.; Meeldijk, J. D.; Evers, W. H.; De Nijs, B.; Boneschanscher, M. P.; De Jongh, P. E.; Verkleij, A. J.; De Jong, K. P.; Van Blaaderen, A.; Vanmaekelbergh, D. Quantitative Structural Analysis of Binary Nanocrystal Superlattices by Electron Tomography. *Nano Lett.* **2009**, *9*(7), 2719–2724. https://doi.org/10.1021/nl901212m.
(13) Schuller, I. K. New Class of Layered Materials. *Phys. Rev. Lett.* **1980**, *44* (24), 1597–1600. https://doi.org/10.1103/PhysRevLett.44.1597.

(14) Segmüller, A.; Blakeslee, A. E. X-Ray Diffraction from One-Dimensional Superlattices in GaAs$_{1-x}$P$_x$ Crystals. *J. Appl. Crystallogr.* **1973**, *6* (1), 19–25. https://doi.org/10.1107/s0021889873007995.

(15) Clemens, B. M.; Gay, J. G. Effect of Layer-Thickness Fluctuations on Superlattice Diffraction. *Phys. Rev. B* **1987**, *35* (17), 9337–9340. https://doi.org/10.1103/PhysRevB.35.9337.

(16) Fullerton, E. E.; Schuller, I. K.; Vanderstraeten, H.; Bruynseraede, Y. Structural Refinement of Superlattices from X-Ray Diffraction. *Phys. Rev. B* **1992**, *45* (16), 9292–9310. https://doi.org/10.1103/PhysRevB.45.9292.

(17) Holý, V.; Pietsch, U.; Baumbach, T. *High-Resolution X-Ray Scattering from Thin Films and Multilayers*; Springer Berlin Heidelberg, 1999. https://doi.org/10.1007/bfb0109385.

(18) Bertolotti, F.; Protesescu, L.; Kovalenko, M. V.; Yakunin, S.; Cervellino, A.; Billinge, S. J. L.; Terban, M. W.; Pedersen, J. S.; Masicocchi, N.; Guagliardi, A. Coherent Nanotwins and Dynamic Disorder in Cesium Lead Halide Perovskite Nanocrystals. *ACS Nano* **2017**, *11* (4), 3819–3831. https://doi.org/10.1021/acsnano.7b00017.

(19) Imran, M.; Ijaz, P.; Baranov, D.; Goldoni, L.; Petralanda, U.; Akkerman, Q.; Abdelhady, A. L.; Prato, M.; Bianchini, P.; Infante, I.; Manna, L. Shape Pure, Nearly Monodisperse CsPbBr$_3$ Nanocubes Prepared Using Secondary Aliphatic Amines. *Nano Lett.* **2018**, *18* (12), 7822–7831. https://doi.org/10.1021/acs.nanolett.8b03598.

(20) Brennan, M. C.; Toso, S.; Pavlovetc, I. M.; Zhukovskyi, M.; Marras, S.; Kuno, M.; Manna, L.; Baranov, D. Superlattices Are Greener on the Other Side: How Light Transforms Self-Assembled Mixed Halide Perovskite Nanocrystals. *ACS Energy Lett.* **2020**, *5* (5), 1465–1473. https://doi.org/10.1021/acsenergylett.0c00630.

(21) Toso, S.; Baranov, D.; Giannini, C.; Marras, S.; Manna, L. Wide-Angle X-Ray Diffraction Evidence of Structural Coherence in CsPbBr$_3$ Nanocrystal Superlattices. *ACS Mater. Lett.* **2019**, *1* (2), 272–276. https://doi.org/10.1021/acsmaterialslett.9b00217.

(22) Tong, Y.; Yao, E. P.; Manzi, A.; Bladt, E.; Wang, K.; Döbleringer, M.; Bals, S.; Müller-Buschbaum, P.; Urban, A. S.; Polavarapu, L.; Feldmann, J. Spontaneous Self-Assembly of Perovskite Nanocrystals into Electronically Coupled Supercrystals: Toward Filling the Green Gap. *Adv. Mater.* **2018**, *30* (29), 1801117. https://doi.org/10.1002/adma.201801117.

(23) Rainò, G.; Becker, M. A.; Bodnarchuk, M. I.; Mahrt, R. F.; Kovalenko, M. V.; Stöferle, T. Superfluorescence from Lead Halide Perovskite Quantum Dot Superlattices. *Nature* **2018**, *563* (7733), 671–675. https://doi.org/10.1038/s41586-018-0683-0.

(24) Sevenhans, W.; Gijs, M.; Bruynseraede, Y.; Homma, H.; Schuller, I. K. Cumulative Disorder and X-Ray Line Broadening in Multilayers. *Phys. Rev. B* **1986**, *34* (8), 5955–5958. https://doi.org/10.1103/PhysRevB.34.5955.

(25) Stoumpos, C. C.; Malliakas, C. D.; Peters, J. A.; Liu, Z.; Sebastian, M.; Im, J.; Chasapis, T. C.; Wibowo, A. C.; Chung, D. Y.; Freeman, A. J.; Wessels, B. W.; Kanatzidis, M. G. Crystal Growth of the Perovskite Semiconductor CsPbBr$_3$: A New Material for High-Energy Radiation Detection. *Cryst. Growth Des.* **2013**, *13*
(7), 2722–2727. https://doi.org/10.1021/cg400645t.

(26) Cottingham, P.; Brutchey, R. L. Depressed Phase Transitions and Thermally Persistent Local Distortions in CsPbBr$_3$ Quantum Dots. *Chem. Mater.* 2018, 30 (19), 6711–6716. https://doi.org/10.1021/acs.chemmater.8b02295.

(27) Yu, Y.; Jain, A.; Guillaussier, A.; Voggu, V. R.; Truskett, T. M.; Smilgies, D. M.; Korgel, B. A. Nanocrystal Superlattices That Exhibit Improved Order on Heating: An Example of Inverse Melting? *Faraday Discuss.* 2015, 181 (0), 181–192. https://doi.org/10.1039/c5fd00006h.

(28) Rodová, M.; Brožek, J.; Knížek, K.; Nitsch, K. Phase Transitions in Ternary Caesium Lead Bromide. *J. Therm. Anal. Calorim.* 2003, 71 (2), 667–673. https://doi.org/10.1023/A:1022836800820.

(29) Bekenstein, Y.; Koscher, B. A.; Eaton, S. W.; Yang, P.; Alivisatos, A. P. Highly Luminescent Colloidal Nanoplates of Perovskite Cesium Lead Halide and Their Oriented Assemblies. *J. Am. Chem. Soc.* 2015, 137 (51), 16008–16011. https://doi.org/10.1021/jacs.5b11199.

(30) Sichert, J. A.; Tong, Y.; Mutz, N.; Vollmer, M.; Fischer, S.; Milowska, K. Z.; García Cortadella, R.; Nickel, B.; Cardenas-Daw, C.; Stolarczyk, J. K.; Urban, A. S.; Feldmann, J. Quantum Size Effect in Organometal Halide Perovskite Nanoplatelets. *Nano Lett.* 2015, 15 (10), 6521–6527. https://doi.org/10.1021/acs.nanolett.5b02985.

(31) Morgenstern, T.; Lampe, C.; Naujoks, T.; Jurow, M.; Liu, Y.; Urban, A. S.; Brütting, W. Elucidating the Performance Limits of Perovskite Nanocrystal Light Emitting Diodes. *J. Lumin.* 2020. https://doi.org/10.1016/j.jlumin.2019.116939.

(32) Dahl, J. C.; Wang, X.; Huang, X.; Chan, E. M.; Alivisatos, A. P. Elucidating the Weakly Reversible Cs-Pb-Br Perovskite Nanocrystal Reaction Network with High-Throughput Maps and Transformations. *J. Am. Chem. Soc.* 2020. https://doi.org/10.1021/jacs.0c03577.

(33) Akkerman, Q. A.; García, B. M.; Buha, J.; Almeida, G.; Toso, S.; Marras, S.; Bonaccorso, F.; Petralanda, U.; Infante, I.; Manna, L. Ultrathin Orthorhombic PbS Nanosheets. *Chem. Mater.* 2019. https://doi.org/10.1021/acs.chemmater.9b02914.

(34) Van Der Meer, B.; Van Damme, R.; Dijkstra, M.; Smallenburg, F.; Filion, L. Revealing a Vacancy Analog of the Crowdion Interstitial in Simple Cubic Crystals. *Phys. Rev. Lett.* 2018, 121 (25). https://doi.org/10.1103/PhysRevLett.121.258001.
(38) Paneth, H. R. The Mechanism of Self-Diffusion in Alkali Metals. Phys. Rev. 1950, 80 (4), 708–711. https://doi.org/10.1103/PhysRev.80.708.

(39) Kato, T.; Iwata, S.; Kokuryu, M.; Tsunashima, S. Perpendicular Magnetic Anisotropy and Magneto-Optical Spectra of MBE Grown MnPt3/Co Multilayers. J. Magn. Soc. Japan 1998, 22 (S2), 85–88. https://doi.org/10.3379/jmsjmag.22.s2_85.

(40) Huang, T. C.; Toraya, H.; Blanton, T. N.; Wu, Y. X-Ray Powder Diffraction Analysis of Silver Behenate, a Possible Low-Angle Diffraction Standard. J. Appl. Crystallogr. 1993, 26 (pt 2), 180–184. https://doi.org/10.1107/S0021889892009762.

(41) Smith, M. D.; Connor, B. A.; Karunadasa, H. I. Tuning the Luminescence of Layered Halide Perovskites. Chemical Reviews. 2019, pp 3104–3139. https://doi.org/10.1021/acs.chemrev.8b00477.

(42) Abécassis, B.; Tessier, M. D.; Davidson, P.; Dubertret, B. Self-Assembly of CdSe Nanoplatelets into Giant Micrometer-Scale Needles Emitting Polarized Light. Nano Lett. 2014, 14 (2), 710–715. https://doi.org/10.1021/nl4039746.

(43) Guzelturk, B.; Erdem, O.; Olutas, M.; Kelestemur, Y.; Demir, H. V. Stacking in Colloidal Nanoplatelets: Tuning Excitonic Properties. ACS Nano 2014, 8 (12), 12524–12533. https://doi.org/10.1021/nn5053734.

(44) Hazarika, A.; Fedin, I.; Hong, L.; Guo, J.; Srivastava, V.; Cho, W.; Coropceanu, I.; Portner, J.; Diroll, B. T.; Philbin, J. P.; Rabani, E.; Klie, R.; Talapin, D. V. Colloidal Atomic Layer Deposition with Stationary Reactant Phases Enables Precise Synthesis of “Digital” II-VI Nano-Heterostructures with Exquisite Control of Confinement and Strain. J. Am. Chem. Soc. 2019, 141 (34), 13487–13496. https://doi.org/10.1021/jacs.9b04866.

(45) Yang, H.; Liang, A.; Chen, C.; Schroeter, N. B. M.; Chen, Y. Visualizing Electronic Structures of Quantum Materials by Angle-Resolved Photoemission Spectroscopy. Nature Reviews Materials. 2018, pp 341–353. https://doi.org/10.1038/s41578-018-0047-2.

(46) Lu, C.; Wright, M. W.; Ma, X.; Li, H.; Itanze, D. S.; Carter, J. A.; Hewitt, C. A.; Donati, G. L.; Carroll, D. L.; Lundin, P. M.; Geyer, S. M. Cesium Oleate Precursor Preparation for Lead Halide Perovskite Nanocrystal Synthesis: The Influence of Excess Oleic Acid on Achieving Solubility, Conversion, and Reproducibility. Chem. Mater. 2019, 31 (1), 62–67. https://doi.org/10.1021/acs.chemmater.8b04876.

(47) Imran, M.; Caligiuri, V.; Wang, M.; Goldoni, L.; Prato, M.; Krahne, R.; De Trizio, L.; Manna, L. Benzoyl Halides as Alternative Precursors for the Colloidal Synthesis of Lead-Based Halide Perovskite Nanocrystals. J. Am. Chem. Soc. 2018, 140 (7), 2656–2664. https://doi.org/10.1021/jacs.7b13477.

(48) Altamura, D.; Lassandro, R.; Vittoria, F. A.; De Caro, L.; Siliqi, D.; Ladisa, M.; Giannini, C. X-Ray Microimaging Laboratory (XMI-LAB). J. Appl. Crystallogr. 2012, 45 (4), 869–873. https://doi.org/10.1107/S0021889812025733.

(49) Siliqi, D.; De Caro, L.; Ladisa, M.; Scattarella, F.; Mazzone, A.; Altamura, D.; Sibillano, T.; Giannini, C. SUNBIM: A Package for X-Ray Imaging of Nano- and Biomaterials Using SAXS, WAXS, GISAXS and GIWAXS Techniques. J. Appl. Crystallogr. 2016, 49 (3), 1107–1114. https://doi.org/10.1107/S1600576716006932.

(50) Tate, M. P.; Urade, V. N.; Kowalski, J. D.; Wei, T. C.; Hamilton, B. D.; Eggiman, B. W.; Hillhouse, H. W.
Simulation and Interpretation of 2D Diffraction Patterns from Self-Assembled Nanostructured Films at Arbitrary Angles of Incidence: From Grazing Incidence (above the Critical Angle) to Transmission Perpendicular to the Substrate. *J. Phys. Chem. B* **2006**, *110* (20), 9882–9892. https://doi.org/10.1021/jp0566008.

(51) Jiang, Z. GIXSGUI: A MATLAB Toolbox for Grazing-Incidence X-Ray Scattering Data Visualization and Reduction, and Indexing of Buried Three-Dimensional Periodic Nanostructured Films. *J. Appl. Crystallogr.* **2015**, *48* (3), 917–926. https://doi.org/10.1107/S1600576715004434.