Bulk and Nanocrystalline Cesium Lead-Halide Perovskites as Seen by Halide Magnetic Resonance

Laura Piveteau, Marcel Aebl, Nuri Yazdani, Marthe Millen, Lukas Korosec, Franziska Krieg, Bogdan M. Benin, Viktoria Morad, Christophe Piveteau, Toni Shiroka, Alex Comas-Vives, Christophe Copéret, Aaron M. Lindenberg, Vanessa Wood, René Verel,* and Maksym V. Kovalenko*

ABSTRACT: Lead-halide perovskites increasingly mesmerize researchers because they exhibit a high degree of structural defects and dynamics yet nonetheless offer an outstanding (opto)electronic performance on par with the best examples of structurally stable and defect-free semiconductors. This highly unusual feature necessitates the adoption of an experimental and theoretical mindset and the reexamination of techniques that may be uniquely suited to understand these materials. Surprisingly, the suite of methods for the structural characterization of these materials does not commonly include nuclear magnetic resonance (NMR) spectroscopy. The present study showcases both the utility and versatility of halide NMR and NQR (nuclear quadrupole resonance) for probing the structure and structural dynamics of CsPbX$_3$ ($X = \text{Cl, Br, I}$), in both bulk and nanocrystalline forms. The strong quadrupole couplings, which originate from the interaction between the large quadrupole moments of, e.g., the $^{35}\text{Cl}$, $^{79}\text{Br}$, and $^{127}\text{I}$ nuclei, and the local electric-field gradients, are highly sensitive to subtle structural variations, both static and dynamic. The quadrupole interaction can resolve structural changes with accuracies commensurate with synchrotron X-ray diffraction and scattering. It is shown that space-averaged site-disorder is greatly enhanced in the nanocrystals compared to the bulk, while the dynamics of nuclear spin relaxation indicates enhanced structural dynamics in the nanocrystals. The findings from NMR and NQR were corroborated by ab initio molecular dynamics, which point to the role of the surface in causing the radial strain distribution and disorder. These findings showcase a great synergy between solid-state NMR or NQR and molecular dynamics simulations in shedding light on the structure of soft lead-halide semiconductors.

INTRODUCTION

Lead-halide perovskites are a class of intensely studied semiconductors with the general formula APbX$_3$ [A = methylammonium (MA), formamidinium (FA), or cesium, X = halide], wherein the cation A is situated in the cuboctahedral voids of a 3D-network of corner-sharing PbX$_6$ octahedra. Various perovskite polymorphs can be derived by octahedral tilting, e.g., by deviating the Pb–X–Pb angle from 180°, as exemplified by the unit cell of γ-CsPbX$_3$ (orthorhombic, Pbam space group, Figure 1a; for all APbX$_3$ compounds see Note S1). In the past five years, these compounds have gained prominence with the demonstration of highly efficient photovoltaics with perovskites as absorber layers,$^{1,2}$ power conversion efficiencies of up to 25.2% have been reported, exceeding those of more traditional semiconductors.$^3$ Moreover, the exceptional optoelectronic characteristics of perovskites are in great demand for other applications, which range from light-emitting devices$^4$ to hard-radiation detectors.$^5$ The past few years have seen a gradual transition from the use of solution-processable MAPbX$_3$ compounds to more chemically robust FAPbX$_3$ as well as CsPbX$_3$ and mixed Cs–FA variants.
There is an increasing body of experimental and theoretical evidence that the soft lattices of these halides favor many of their unusual characteristics\textsuperscript{14–18} for instance, the intrinsic formation of polarons can screen charge carriers from defects and increase charge carrier lifetimes, aiding exciton and charge carrier cooling, and yielding unusually high dielectric constants.

Solid-state nuclear magnetic resonance (NMR) spectroscopy of inorganic materials serves as a valuable addition to the suite of more conventional characterization tools (diffraction techniques, electron microscopy, etc.). In the limit of highly disordered materials, NMR may even be a unique gateway to the interpretation of NMR spectra. For small-to-intermediate quadrupole interactions (e.g.,\textsuperscript{35/37}Cl in perovskites), a second order perturbation approach is sufficient to lift the degeneracy of spin energy states with a large enough nuclear quadrupole moment (see Table S2), which couple with the electric-field gradient (EFG) generated by neighboring nuclei and electrons. This coupling, known as the quadrupole interaction, allows the structure and dynamic properties of inorganic materials to be probed with both NMR and NQR. (c) Simulations of the \textsuperscript{127}I NMR and NQR spectra for bulk \gamma-CSnPbI\textsubscript{3} powder by an exact description of the spin Hamiltonian and powder averaging. The quadrupole parameters used for the simulations are the ones reported later in this work. Details about how the simulation was performed are provided in the Methods section.

In NMR spectroscopy, the Zeeman interaction (\(H_0\)) lifts the degeneracy of the spin states in a magnetic field. The nuclear-spin transitions scale linearly with the magnetic field strength and are characterized by the Larmor frequency, \(\omega_0\). Deviations from the Larmor frequency are induced by the electric–dipole coupling, and the interpretation of NMR spectra. For small-to-intermediate quadrupole interactions such as the chemical shift, the dipole–dipole coupling, and \(H_Q\) (Figure 1b). In general, these interactions are anisotropic in nature, and especially large quadrupole interactions can produce broad NMR signals (tens to hundreds MHz in width), reduced resolution, and complex line shapes. All these factors complicate the signal acquisition and the interpretation of NMR spectra. For small-to-intermediate quadrupole interactions (e.g.,\textsuperscript{35/37}Cl in perovskites), a second order perturbation approach is sufficient to describe the spin system\textsuperscript{38,39}. However, strong quadrupole interactions, in the range of several tens to hundreds MHz (e.g., \textsuperscript{125}I in perovskites), can be comparable to or even stronger than \(H_{EFG}\) and result in a breakdown of the perturbation approximation. The exact calculation of the spectral features is required to interpret the NMR spectra.\textsuperscript{40} However, with a large \(H_Q\), the energy transitions can be studied using nuclear quadrupole resonance (NQR). NQR is performed on the same hardware as NMR, but in absence of an applied magnetic field. The EFG leads to spin-energy splitting in the form of the quadrupole interaction, as illustrated by the example of a spin \(I = 5/2\) (\textsuperscript{125}I in Figure 1b).

The simulated NMR and NQR spectra of \gamma-CSnPbI\textsubscript{3} (Figure 1c) demonstrate the advantages of NQR over NMR for...
quadrupolar nuclei such as $^{127}$I, $^{129}$I NMR spectroscopy is highly impractical with present-day commercial spectrometers. On the other hand, because of the large $H_Q$ of $^{127}$I, NQR can be performed, and the simulated NQR spectrum of $\gamma$-CsPbI$_3$ consists of only four lines at distinct frequencies, suggesting that $^{127}$I NQR may serve as a highly practical characterization tool for lead iodide perovskite materials. Note S2 further discusses the basics and experimental aspects of NMR and NQR spectroscopy for halide nuclei.

Here, we study bulk and nanocrystalline CsPbX$_3$ materials at various temperatures with NMR and NQR spectroscopies. We perform $^{35}$Cl and $^{79}$Br NMR spectroscopy, which are the first reported halide NMR studies of the APbX$_3$ family in both bulk and nanocrystalline forms. For nuclei with larger quadrupole moments like $^{79}$Br, and especially $^{127}$I, we showcase the use of pure NQR spectroscopy. DFT calculations indicate that $^{79}$Br NQR offers structural precision on par with synchrotron X-ray diffraction. The results shed light on structural variations between the samples as well as differences in structure dynamics. While the crystal structures of bulk and nanocrystalline CsPbX$_3$ materials are found to be indistinguishable, the relaxation behavior of the halide spins differs drastically in NCs. With the aid of ab initio molecular dynamics (AIMD) simulations, we relate the accelerated nuclear spin relaxation in NCs to the enhanced anharmonic structure dynamics in these materials.

## RESULTS

CsPbX$_3$ compounds have been reported to crystallize in a range of perovskite Glazer tilting systems and in one nonperovskite phase (Figure 2a; see Note S1 for a crystallographic overview). In the following, we establish the halide magnetic resonance, both NMR and NQR, as versatile tools for studying CsPbX$_3$ in bulk microcrystalline forms (Figure 2b)\(^{11,42}\) and for ligand-capped colloidal NCs (Figure 2b–d).\(^{43}\) Such a comparative study allowed us to probe the effects of structural dynamics\(^{44,45}\) and disorder,\(^{46}\) as well as the surface defects and ligands\(^{47,48}\) The effects of structure dynamics on NMR and NQR spectra at various temperatures are herein corroborated via AIMD simulations.

$^{35}$Cl NMR of Bulk CsPbCl$_3$ and CsPbBr$_3$ NCs. Among the studied halides, the $^{35/37}$Cl nuclei ($I = 3/2$) possess the smallest quadrupole moments and are therefore well-suited for NMR spectroscopy. A small quadrupole moment produces pure NQR lines at very low frequencies and with low intensities (due to low Boltzmann factors), thus making pure NQR rather impractical for chloride perovskites. Since the two chlorine isotopes are chemically and magnetically very similar (see Table S2), we concentrated on the more abundant $^{35}$Cl isotope to study the differences in structure and dynamics between bulk CsPbCl$_3$ powder and CsPbCl$_3$ NCs (8.5 nm edge length), the latter being prepared by the hot-injection method and stabilized with long-chain zwitterionic surface-capping ligands.\(^{39}\) $^{35}$Cl solid-state NMR spectra of bulk and nanocrystalline CsPbCl$_3$ were acquired under static conditions at 100, 150, 200, 250, and 273 K. To avoid inhomogeneous excitation from pulse-shape imperfections, the signals were constructed from three subspectra with different frequency offsets. These were recorded using the wide-band, uniform-rate, and smooth truncation Carr–Parceau–Meiboom–Gill pulse sequence (WURST-CPMG, see the Methods section and the Supporting Information) and processed to obtain the skyline spectra displayed in Figure 3a. The WURST excitation pulses permit the homogeneous excitation of a broad frequency range (1 MHz in this case), while the CPMG part of the pulse sequence refocuses the signal in the time domain leading to signal enhancement in the case of long $T_2$ relaxation times (i.e., slow dephasing of the magnetization response). The $^{35}$Cl NMR spectra of the bulk material are well described by a single, axially symmetric chlorine site with a quadrupole coupling constant ($C_Q$) = 15.48 MHz and quadrupole asymmetry ($\eta_Q$) = 0 (obtained by simulating the spectra using the exact description of the quadrupole interaction, see also Note S3 and Figure S2). The chemical shift anisotropy and other spin interactions were neglected, as the line shape of the spectra was found to be dominated by the quadrupole interaction (Figure S4). At lower temperatures, the Gaussian

---

**Figure 2.** Different crystal phases and forms of CsPbX$_3$. (a) Schemes of the 3D cubic CsPbI$_3$ perovskite structure and the projections along the c-axis of the cubic (α) perovskite structure and the tetragonal (β), orthorhombic (γ), and monoclinic phases derived from it via the tilting of octahedra. The thermodynamically stable phase of CsPbI$_3$ at ambient conditions is the orthorhombic-δ-phase. (b) Different forms of CsPbX$_3$, namely, ligand-capped colloidal NCs (in cuvettes) and microcrystalline powders (in watch glasses), studied in this work. For CsPbI$_3$, both metastable γ-phase and the stable δ-phase are presented. (c) Luminescence of CsPbX$_3$ NC colloids under UV-light. (d) The NCs are cuboid-shaped crystallites of 8–12 nm in size, exemplified by a high-resolution HAADF-STEM image of a single CsPbCl$_3$ NC.
line width increased by almost a factor of 2, and at least one other species became visible below 250 K (a shoulder that grows at higher frequencies, Figure 3d), which may be assigned to one of the three crystallographically inequivalent Cl-species in CsPbCl₃ (in the orthorhombic or monoclinic polymorphs). Quadrupole parameters could not be determined for this signal component due to the lack of resolvable spectral features. The local surrounding of ³⁵Cl spins in NCs and in bulk is very similar (Figure 3a), which is also apparent from the similarity of the quadrupole parameters (15.48 and 15.51/15.49 MHz, respectively, see Figure S2). From the structural viewpoint, the time-averaged orientations of PbCl₆ octahedra are also very similar.

Not only are NC signals broader as compared to bulk, which is expected due to the increased structural disorder (see also the following discussion of the AIMD simulations), but they are also characterized by notably different intensity ratios in the respective left and right horns. In the ³⁵Cl NMR spectra of bulk CsPbCl₃, the right horn of the signal around -5500 ppm (-58.47 MHz) is always taller than the left one at around 3450 ppm (-58.99 MHz). This is usual for the spectra of quadrupolar nuclei on sites with or close to axial symmetry. Conversely, the NC spectra exhibit a left horn which is larger than the right horn. This pattern can be explained by the presence of a distribution of quadrupolar parameters as described by an extended Czjzek statistic or the Maurer model. If disorder leads to a normal distribution of EFGs at a certain crystallographic site, a quadrupolar spin at this position will exhibit an asymmetric line shape tailing toward higher frequencies due to the nonlinear transformation of the EFG tensor into spectroscopic observables. Thus, depending on the nature and the extent of the disorder, the two horns of an axially symmetric tensor may be expected to be of the same height or the left horn might even tower above the right.

The signal-to-noise ratios in the ³⁵Cl NMR spectra of NCs are a factor of 2–35 worse than the equivalent bulk spectra (see Note S4 for details of this estimate). This loss of signal in the NC NMR spectra is mainly due to the rapid loss of coherence in the free-induction-decay (FID) of NCs, which reduces the number of acquirable echoes in the CPMG train and results in lower signal intensity. This is also apparent when comparing the CPMG echo-train decay rates in CsPbCl₃ NCs (T₂ times), which are well described by single-exponential fits (Figure 3c) and are

Figure 3. ³⁵Cl NMR of bulk and nanocrystalline CsPbCl₃. (a) ³⁵Cl NMR static spectra of bulk CsPbCl₃ (black) and CsPbCl₃ NCs (blue) at a field of 14.1 T acquired at temperatures ranging from 100 to 273 K. Below the shift axis in ppm, the absolute resonance frequency axis is indicated in MHz. All the spectra are well described by a single axially symmetric chlorine species. (b, c) Graphs displaying the temperature dependence of ³⁵Cl NMR T₁ and T₂ time constants in bulk CsPbCl₃ (■) and CsPbCl₃ NCs (dark blue ●) under static conditions. Whenever error bars are not visible, they are smaller than the plotted data point. (d) Zoomed-in view of the ³⁵Cl NMR spectra of bulk and nanocrystalline CsPbCl₃ at 100 and 273 K. The zoom facilitates the observation of the shoulder at -6000 ppm in bulk CsPbCl₃, as described in the Results section, and which is assigned to another, crystallographic inequivalent chlorine species, belonging to the monoclinic CsPbCl₃ phase. Due to significant line broadening, the presence of this chlorine species could be neither confirmed nor excluded for CsPbCl₃ NC as it could not be resolved due to site-disorder.
Figure 4. Ab initio calculations of CsPbCl₃ NCs. (a) Atomistic model of a 4.6 nm CsPbCl₃ NC, with a cross-section removed to indicate four regions of interest within the NC, from the outer layers (1) to the central core of the NC (4) (Figure S14). (b) Plots of the statistical distribution of Pb–Cl–Pb angles, α, within each region of the NC. (c) Standard deviation of α as a function of distance of the Cl atom from the surface of the NC, d. The dashed line is a fit, \(\sigma(\alpha) \propto \frac{1}{d^{0.31 (\text{nm})}}\). (d) Plot of the partial phonon density of states in each of the four regions of the NC, normalized to the phonon frequency squared to accentuate the low-energy region. The dashed line is that calculated for bulk CsPbCl₃. (e) Plot of the mean-squared-thermal-displacement, \(\langle u^2 \rangle\), of each atom type in each of the 4 regions of the NC. The dashed lines correspond to the \(\langle u^2 \rangle\) calculated for bulk CsPbCl₃.

The disparity in the behavior of \(T_1\) and \(T_2\) times is surprising, since most relaxation-rate-influencing interactions affect both \(T_1\) and \(T_2\) times. We attribute this difference in the behavior of \(T_2\) vs temperature in the bulk and NCs to dynamic processes, such as chemical exchange in the fast regime, which can produce line broadening, if it influences the spectrum at all. Chemical exchange is a dynamical process whose initial and final states are indistinguishable; it is considered “fast” when its rate greatly exceeds the difference between the magnetic resonance frequencies of the involved chemical species (for more discussion about chemical exchange see Note S5). For these dynamic processes we propose two plausible mechanisms. The first is vacancy-assisted halide-ion mobility, abundantly reported in bulk single-crystals and polycrystalline films, which may be drastically enhanced by surfaces and interfaces. "The reported activation energies for halide-ion migration in perovskites are ca. 100 meV. The existence of a new pathway for ionic motion, e.g., surface ionic mobility with extremely low activation energies, could explain the observed disparity in \(T_1\)-behavior between NCs and bulk. The second, more plausible in our view, is dynamic disorder of the lattice driven by anharmonic dynamics, evidently enhanced in NCs. We then conducted DFT-based structure-optimization and AIMD simulations to elucidate the effects of static structural disorder, which may impact inhomogeneous NMR signal broadening, and dynamic disorder. The latter may explain the chemical exchange seen in the homogeneous line width and peculiar behavior of \(T_2\) times in NCs.

We cut a cesium and halide rich cubic (\(\sim 4.6\) nm) NC out of bulk orthorhombic CsPbCl₃ and performed a full geometry optimization of the NC to find its ground state physical structure (Figure 4a). We find that strain induced by undercoordination of the NC’s surface atoms leads to strong deformations of the lattice at the surface as well as in subsequent layers. This is particularly evident when considering the Pb–Cl–Pb bonding angles (\(\alpha\)) of the structure, as shown in Figure 4b. In the core of the NC, the lattice remains in the orthorhombic phase; however, as one moves toward the surface the distribution of \(\alpha\) significantly broadens and, on average, shifts toward higher angles. These surface induced deformations decay as \(\sigma(\alpha) \propto \frac{1}{d^{0.31 (\text{nm})}}\) (Figure 4c), such that, for the 9.5 nm NCs measured with NMR, \(\sim 60\%\) of the Cl atoms will be within this disordered surface layer. This disorder, which is strongest in the regions close to the surface (regions 1 and 2 in Figure 4) and therefore local disorder of

\[\text{https://dx.doi.org/10.1021/acscentsci.0c00587}\]

ACS Cent. Sci. 2020, 6, 1138–1149
Figure 5. $^{79}$Br NMR and NQR of bulk and nanocrystalline CsPbBr$_3$. (a) Static solid-state $^{79}$Br NMR spectrum at RT for bulk CsPbBr$_3$ constructed from 41 subspectra acquired at 16.4 T (bold, black line). $C_Q = 133.59, 136.36$ MHz; $\eta_Q = 0.006, 0.03$; and $\delta_{\text{iso}} = -312, -147$ ppm are the parameters used to simulate the spectrum (dashed, blue line). At around 29 000 ppm ($-180.5$ MHz), background of the probe that could not be suppressed contributes to the signal (Figure S9). As this spectrum was acquired at a higher magnetic field than the $^{35}$Cl NMR spectra of CsPbCl$_3$ (14.1 T), the quadrupole parameters obtained from simulations are the only means by which comparison of the spectra is possible. (b) $^{79}$Br NQR lines of bulk CsPbBr$_3$ at various temperatures. Higher- and lower-intensity lines correspond, respectively, to equatorial and axial Br atoms, of the orthorhombic structure of CsPbBr$_3$. At 90 K, a single, broad $^{79}$Br NQR signal was found for CsPbBr$_3$ NCs (light blue line). When fitting the NC signal with a Gaussian, it is centered at $-67.12$ MHz compared to $-67.08$ MHz for bulk CsPbBr$_3$. The obtained full widths at half-maximum (fwhm) are 900 and 75 kHz for bulk and nanocrystalline CsPbBr$_3$, respectively. The signal of NCs is inhomogeneously broadened as it was constructed from 42 subspectra acquired with a Hahn echo pulse sequence. (c) Temperature dependence of the $T_1$ times of the two $^{79}$Br NQR lines of bulk CsPbBr$_3$ (low-frequency transition ■, high-frequency transition, dark blue ●). (d) Temperature dependence of the $T_1$ times of the two $^{79}$Br NQR lines of bulk CsPbBr$_3$ acquired with shorter echo delays (20 $\mu$s, low-frequency transition ■, high-frequency transition, dark blue ●) and longer echo delays (110 $\mu$s, low-frequency transition, grey ■; high-frequency transition, light blue ●). Whenever error bars are not visible, they are smaller than the plotted data point.

The EFG, can explain the enhanced inhomogeneous line broadening of the NMR signal in the NCs (Figure 3).

In Figure 4d, we plot the normalized partial phonon density of states $g(\omega)/\omega^2$ in each of the regions of the NC, computed from AIMD (the full $g(\omega)$ is given in the Supporting Information). In the core of the NC, $g(\omega)/\omega^2$ resembles that calculated for bulk CsPbCl$_3$ and at very low energies (<2 meV) is roughly constant. This is consistent with what is expected assuming a linear dispersion of acoustic phonons. Approaching the surface of the NC, we see the emergence of a continuum of low-energy phonon modes along with a strong increase in the mean-squared-thermal-displacement of all Cs, Pb, and Cl atoms, as shown in Figure 4e. These findings indicate the presence of soft phonon-modes in the structurally disordered surface layer of the NC. Soft phonon modes typically arise in the vicinity of a structural phase transition triggering lattice instability and have been characterized around the phase transitions in bulk CsPbCl$_3$ as well as in MAPbI$_3$ and CsPbI$_3$. Dynamically disordered EFGs will result from anharmonic atomic motion in the presence of soft modes and could explain the $T_2$ coherence loss that is observed in bulk CsPbCl$_3$ as the temperature approaches the phase transition at ~RT. In a NC, the soft modes do not result from the proximity to a phase transition, but rather from the flat energy landscape of the structurally disordered surface. Temperature independent $T_2$ coherence loss can thus be expected down to low temperatures, as indeed observed.

$^{79}$Br NMR and NQR of Bulk CsPbBr$_3$ and CsPbBr$_3$ NCs. The spin properties of $^{79/81}$Br nuclear spins (I = 3/2) are comparable, with $^{79}$Br being preferred over $^{81}$Br for its slightly larger quadrupole moment. $^{79}$Br has a quadrupole moment that is half that of $^{127}$I but more than 3 times that of $^{35}$Cl (see Table S2). This has consequences on the $^{79}$Br NMR spectrum, as well as on the ease with which NQR lines can be detected. The $^{79}$Br NMR signal of bulk CsPbBr$_3$ can be characterized by bromine sites close to axial symmetry at RT. However, the frequency span of the CsPbBr$_3$ halide NMR signal is 1 order of magnitude larger than that of bulk CsPbCl$_3$ (NMR spectra in Figures 3a and 5a). Two bromide species with substantially higher quadrupole coupling ($C_Q = 133.59, 136.36$ MHz; $\eta_Q = 0.006, 0.03$) compared to CsPbCl$_3$ can be determined by simulating the spectra. 41 WURST-CPMG subspectra (1 MHz each) with varying frequency offsets were needed to acquire the $^{79}$Br NMR signal of bulk CsPbBr$_3$. This increases the measurement time by at least an order of magnitude to days as compared to the hours required for $^{35}$Cl NMR of CsPbCl$_3$.
79Br NMR spectra of a similar width were found also for bulk MAPbBr3 and FAPbBr3 (Figure S3).

Since we could not detect the 79Br NMR signal for CsPbBr3 NCs, we had to turn to 79Br NQR experiments for a comparative NC vs bulk study. With acquisition times of just a few minutes, a series of 79Br NQR spectra of bulk CsPbBr3 could be easily obtained at various temperatures (Figure 5b). The decrease of the crystal symmetry upon cooling manifests itself in the gradual increase of the separation between NQR lines and their shift to higher absolute frequencies; both effects are due to an increase in CQ and a reduction in the symmetry of the EFG. These findings agree with earlier 79Br and 81Br NQR studies on bulk CsPbBr3 as well as bulk MAPbBr3. The NQR signal of CsPbBr3 NCs was obtained by performing low-temperature 79Br NQR experiments at 90 K using a homemade spectrometer. Only a weak signal was found, which was centered at −67.12 MHz with a full width at half-maximum (fwhm) of 900 kHz (Figure 5b), and no signal was found at lower frequencies (down to −76.66 MHz). The center of the NQR line is slightly shifted relative to that of bulk CsPbBr3 (−67.08 MHz, fwhm = 75 kHz). The large width of the 79Br NQR resonance from NCs indicates a much larger distribution of EFGs and precludes an unambiguous assignment of the lattice structure to orthorhombic, tetragonal, or cubic perovskite polymorphs. This agrees well with the commonplace reports on structural disorder in NCs. Twinned orthorhombic subdomains were proposed based on X-ray scattering analysis. An alternative description could invoke the polymorphous nature of perovskite materials and, as already discussed above for CsPbCl3 NCs, the radial gradient of octahedral tilt angles. The DFT-based structural optimization of a ∼4.6 nm CsPbBr3 NC, identical to that performed for the CsPbCl3 NC above, confirms that the structural disorder of the NC surface also occurs to a similar extent in CsPbBr3 NCs (see Figure S10). DFT calculations indicate that the quadrupole parameters, and hence the NQR signal frequencies, are strongly influenced by minute structural changes. Changing the lattice parameters of orthorhombic CsPbBr3 by just thousandths of an Angstrom will lead to changes in CQ of a few tens of kHz (see Note S6). This is several orders of magnitude above the sub-Hz resolution limit of modern magnetic resonance spectrometers. In other words, the high sensitivity of NMR and NQR to quadrupole interaction allows, at least theoretically, resolutions that are comparable to that of synchrotron X-ray diffraction.

The analysis of 79Br NQR T1 and T2 relaxation times of bulk CsPbBr3 (Figure 5c,d) shows that they are further enhanced (by 1−2 orders of magnitude) compared to T1 and T2 times in 35Cl NMR of bulk CsPbCl3. Reasoning by analogy, the relaxation times of CsPbBr3 NCs are expected to be 1−2 orders of magnitude shorter than the one found in CsPbCl3 NCs. Hence, we expect the short T2 times of CsPbBr3 NCs (ca. 50−500 μs) to impede successful detection of the 79Br NQR signal. This might explain the extremely weak signal at 90 K (Figure 5b). Chemical exchange is also readily observable in bulk CsPbBr3 at roughly the same rate (0.1−2.4 ms) as for CsPbCl3. This was again determined by the 79Br NQR signal dependence on the echo-delay times used in the CPMG echo-train experiments (Figure 5d). AIMD simulations of the CsPbBr3 NC indicate the emergence of low-energy soft phonons in the structurally disordered surface layer of the NC, analogous to the findings for the CsPbCl3 NC (see Figure S11). Similar chemical exchange rates resulting from anharmonic structural deformations on the surface of the CsPbBr3 NC can therefore be expected.
$^{127}$I NQR of Bulk CsPbI$_3$ and CsPbI$_3$ NCs and Discussion about $^{127}$I NMR. Having $I = S/2$, $^{127}$I is the only halide nucleus whose quadrupole parameters, $C_Q$ and $\eta_Q$, can be entirely determined with NQR as its spectrum contains the minimum number of required transitions (two). Furthermore, iodine is among the 10 chemical elements which possess the largest quadrupole moments, and it is also the nucleus with the largest quadrupole couplings in this study. While these characteristics make $^{127}$I NMR spectroscopy on CsPbI$_3$ impractical (see detailed discussion in Note S2), they are ideal for $^{127}$I NQR experiments.

The thermodynamically stable RT polymorph of bulk CsPbI$_3$ is the yellow $\delta$-phase with the nonperovskite, NH$_4$CdCl$_3$ structure, which is composed of 1D-chains of edge-sharing PbI$_6$ octahedra (Figure 2a). The $^{127}$I NQR spectrum of this material consists of four transitions (Figure S5). Following Volkov et al., we grouped these four lines into two pairs ($-124.9071$ and $-70.0794$ MHz, and $-92.9890$ and $-56.1744$ MHz) and extracted the corresponding quadrupole parameters of $C_Q = 424.3$ MHz and $\eta_Q = 0.311$, and $C_Q = 319.7$ MHz and $\eta_Q = 0.4148$ (Figure S5). These values deviate only slightly from those in ref 68. The assignment of these NQR resonance pairs to specific crystallographic iodine sites is nontrivial, and to this end, DFT calculations of the EFG tensors are required. The simpler approach of assigning signals based on NQR line intensities is involved as not only does the Boltzmann statistic need to be considered, but also the flatness of response of the spectrometer must be evaluated.

The crystal structure of the perovskite $\gamma$-CsPbI$_3$ phase comprises a 3D-network of corner-sharing octahedra. However, this phase is metastable at ambient conditions and transforms spontaneously into the above-described yellow $\delta$-phase in the course of hours/days (bulk material) to weeks (NCs). Four lines were found at $-160.88$, $-155.34$, $-81.50$, and $-77.75$ MHz for bulk $\gamma$-CsPbI$_3$ (Figure 6a), corresponding to two iodine sites with quadrupole parameters $C_Q = 517.98$ and $537.36$ MHz, and $\eta_Q = 0.025$ and 0.101 (Table S4). The NQR spectrum of colloidal CsPbI$_3$ NCs (8 nm edge length, synthesized as described in ref 49) coincides with the NQR lines of $\gamma$-CsPbI$_3$ (Figure 6), confirming that NCs crystallize in the same polymorph, as found by XRD. We note that if these NCs would have crystallized in the cubic polymorph ($\alpha$-CsPbI$_3$), as sometimes reported in the literature, the NQR spectrum would have contained only two lines (one species). Although the NQR line width is not broadened compared to the bulk counterpart (as in the case of CsPbBr$_3$ NCs), the $T_2$ times become much shorter (see Table S4). $T_2$ times of CsPbI$_3$ NCs could not be evaluated due to the excessive number of scans required to obtain a sufficient signal-to-noise ratio (131 072 scans per subspectrum). Besides the fast $T_2$ relaxation, the acquisition was further hampered by a strong background signal (Figure S13).

### CONCLUSIONS

We have demonstrated that the large quadrupole interaction of halide nuclear spins is a sensitive probe for studying bulk and nanocrystalline CsPbX$_3$ (X = Cl, Br, I) by means of NMR ($^{35}$Cl, $^{79}$Br) and NQR ($^{79}$Br, $^{127}$I) spectroscopy. The use of NMR or NQR spectroscopy is mostly dictated by the size of the quadrupole coupling relative to the Larmor frequency, since the structural and dynamical information contained in the EFG is accessible by both methods. These techniques readily distinguish between various perovskite polymorphs, and they reveal increased structural disorder and faster chemical exchange in NCs. The latter was attributed to structure dynamics occurring on the time scale of a few milliseconds or faster. From AIMD simulations, we propose that the increased $T_2$ relaxation rates in NCs originate from the anharmonic dynamics driven by low-energy soft-modes, whereas the increased inhomogeneous line broadening might reflect the increased structural disorder that occurs within the surface region. This region constitutes the majority of the NC’s volume (when NCs do not exceed 10 nm). We would like to emphasize that NQR spectroscopy is a readily accessible technique as there is no need for a magnet (the most costly component of high-field NMR spectrometers) and that it retains, encoded in its signal, the equivalent information about the material’s structure and dynamics. Future studies should focus on further developing and applying halide NMR and NQR spectroscopy to the broader compositional and structural space of metal halides, beyond lead-halide perovskites as well as their diverse forms and morphologies (thin films, single-crystals, amorphous, or matrix embedded). We would also emphasize that NQR is readily applicable to investigate metal-halide materials already integrated within a device (such as solar cells) as NQR has either no or only minimal restrictions on electronic conductivity, the presence of other materials, or sample size, and it does not require sample spinning.

### METHODS

#### Sample Syntheses.

Bulk CsPbCl$_3$, CsPbBr$_3$, and CsPbI$_3$ were grown from solvents, whereas $\gamma$-CsPbI$_3$ was obtained via solid-state synthesis. CsPbCl$_3$ and CsPbBr$_3$ NCs were obtained by the hot-injection method using zwitterionic ligands, while CsPbI$_3$ NCs were synthesized using oleic acid and oleylamine ligands. See further details in the Supporting Information.

#### Solid-State NMR Spectroscopy.

$^{35}$Cl and $^{79}$Br NMR experiments were conducted on a wide-bore Bruker 14.1 T and a standard-bore 16.4 T NMR spectrometer, respectively. Both were equipped with Avance III HD consoles. A double resonance 3.2 mm low-temperature MAS probe and a double resonance 4 mm MAS probe were used, respectively. Variable temperatures were reached with a low-temperature-control cabinet using liquid nitrogen as a cooling medium. All equipment was from Bruker Switzerland AG, Fällanden.

Halide NMR signals were acquired under static conditions, stepwise, by moving the carrier frequency. The spectra were constructed by taking the skyline of the subspectra. A WURST-CPMG pulse sequence was applied as described by O’Dell and Schurko, using WURST-80 pulses (50 $\mu$s length, 1000 points, 1 MHz frequency width from low to high frequencies).

$^{35}$Cl NMR $T_1$ times were obtained by fitting the signal integral versus increasing recovery delay. The individual spectra at every value of recovery delay were acquired using the same WURST-CPMG pulse sequence as for spectral acquisition. Except for the recovery delay time, experimental conditions were identical for all experiments.

$^{35}$Cl NMR $T_2$ times were extracted from CPMG echo trains of the subspectra of the overall NMR signal by evaluating the integral of the individual echoes and fitting their evolution during the time of an FID.

Chemical shifts were referenced to 0.1 M NaCl in $D_2$O and 0.01 M NaBr in $D_2$O.
**NQR Spectroscopy.** $^{79}$Br NQR lines and $T_1$ times at various temperatures were recorded on a setup consisting of a home-built spectrometer (described elsewhere) and a single-channel probe head with $Q \sim 100$. The probe could be cooled from RT down to $\sim 5$ K by using a continuous-flow (CF-1200) helium cryostat (Oxford Instruments). $^{79}$Br NQR lines were acquired under static conditions by performing Hahn spin–echo experiments at various carrier frequencies and by taking the skyline of the subspectra. A stepwise data acquisition was required due to the narrow excitation width of the pulses, enforced by the risk of electrical discharges in the helium atmosphere.

$^{79}$Br NQR $T_1$ times at various temperatures were recorded using saturation recovery experiments at both $^{79}$Br NQR frequencies.

$^{79}$Br NQR $T_2$ times were recorded on a double resonance 3.2 mm low-temperature MAS probe conceived for a wide-bore Bruker 14.1 T NMR spectrometer, connected to an Avance III HD console and placed outside the NMR magnet (low external magnetic field, ca. 80 $\mu$T). $T_2$ times were evaluated from echo-trains obtained with the conventional QCPMG Bruker pulse sequence. $^{127}$I NQR frequencies and relaxation times were acquired on a double-resonance 4 mm MAS probe conceived for a standard bore 11.7 T Bruker NMR spectrometer, connected to an Avance III HD console and placed outside the NMR magnet (low external magnetic field, ca. 80 $\mu$T). The $^{127}$I NQR spectra were obtained under static conditions by performing Hahn echo experiments at various carrier frequencies and taking the skyline of the subspectra. The narrow excitation width of the pulses required stepwise acquisition. For CsPbI$_3$ NCs the background was measured with a rotor containing glycine at frequencies. Corrections from Faraday magnetization and the mass-weighted position correlation function, $f(t)$:

$$g_2(t) = m_i \omega^2 |\mathcal{F}[r_i(t)]|^2 \frac{\hbar \omega}{k_B T} (1 + (\epsilon \hbar \omega/k_B T - 1)^{-1}),$$

where the sum is over all atoms in the NC, $m_i$ is the mass of atom $i$, and $\mathcal{F}\{\ldots\}$ is a Fourier transform. Further details and discussions of the calculations are provided in the Supporting Information.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscentsci.0c00587.

Additional methods, data, and figures including crystal structures, NMR properties, NMR and NQR data, ab initio calculations, phonon density of states, DFT calculations, HAADF-STEM image, and TEM images (PDF)

**AUTHOR INFORMATION**

**Corresponding Authors**

René Verel — Department of Chemistry and Applied Biosciences, ETH Zürich, Zürich CH-8093, Switzerland; orcid.org/0000-0003-1575-2232; Email: verelr@ethz.ch

Maksym V. Kovalenko — Department of Chemistry and Applied Biosciences, ETH Zürich, Zürich CH-8093, Switzerland; Empa-Swiss Federal Laboratories for Materials Science and Technology, Dübendorf, Dübendorf CH-8600, Switzerland; orcid.org/0000-0002-6396-8938; Email: mvkovalenko@ethz.ch

**Authors**

Laura Piveteau — Department of Chemistry and Applied Biosciences, ETH Zürich, Zürich CH-8093, Switzerland; Empa-Swiss Federal Laboratories for Materials Science and Technology, Dübendorf, Dübendorf CH-8600, Switzerland; orcid.org/0000-0001-6275-5116

Marcel Aebli — Department of Chemistry and Applied Biosciences, ETH Zürich, Zürich CH-8093, Switzerland; Empa-Swiss Federal Laboratories for Materials Science and Technology, Dübendorf, Dübendorf CH-8600, Switzerland; orcid.org/0000-0002-6460-8336

Nuri Yazdani — Department of Information Technology and Electrical Engineering, ETH Zürich, Zürich CH-8092, Switzerland; Department of Materials Science and Engineering, Stanford University, Stanford, California 94305, United States; orcid.org/0000-0001-6593-7601

Marthe Millen — Department of Chemistry and Applied Biosciences, ETH Zürich, Zürich CH-8093, Switzerland

Lukas Korosoc — Department of Physics, ETH Zürich, Zürich CH-8093, Switzerland

Franziska Krieg — Department of Chemistry and Applied Biosciences, ETH Zürich, Zürich CH-8093, Switzerland; Empa-Swiss Federal Laboratories for Materials Science and Technology, Dübendorf, Dübendorf CH-8600, Switzerland; orcid.org/0000-0002-0370-1318

Bogdan M. Benin — Department of Chemistry and Applied Biosciences, ETH Zürich, Zürich CH-8093, Switzerland; Empa-Swiss Federal Laboratories for Materials Science and Technology, Dübendorf, Dübendorf CH-8600, Switzerland; orcid.org/0000-0002-6502-8237

**Simulation and Data Processing.** Simulations and data processing were performed with custom-written MATLAB codes incorporating functions from the matNMR toolbox by Jacco van Beek. The Hamiltonians of the spin systems were constructed in the matrix representation and diagonalized numerically. Only the Zeeman and the quadrupole Hamiltonians were considered as other spin interactions are weak in comparison (Figure S4). Since $\nu_Q \gg \nu_\omega$, the transition amplitudes of the resonances can be deduced as described in the literature. Spectra were constructed by evaluating the energy levels for a representative number (100 000) of crystallites’ orientations within a powder (powder averaging). Corrections from Faraday’s law and Boltzmann-statistics were neglected in the computation of the spectra.

A detailed description of the data processing of individual spectra is provided in the Supporting Information. The codes are made available from the authors upon request.

**Ab Initio Calculations of NCs.** Ab initio calculations were performed within the CP2K program suite. For bulk calculations, cell optimizations of the orthorhombic unit cell were first performed, with convergence to 1 bar. AIMD simulations were performed in the NVT ensemble at 300 K. The phonon density of states, $\omega_i(t)$, along with the partial density of states for each atom type, $\omega_j(t)$, were computed from the atomic trajectories, though the power spectrum of the mass-weighted position correlation function, $r_i(t)$:
Viktoria Morad — Department of Chemistry and Applied Biosciences, ETH Zürich, Zürich CH-8093, Switzerland; Empa-Swiss Federal Laboratories for Materials Science and Technology, Dübendorf, Dübendorf CH-8600, Switzerland

Christophe Piveteau — Department of Physics, ETH Zürich, Zürich CH-8093, Switzerland

Toni Shiroka — Department of Physics, ETH Zürich, CH-8093, Switzerland; Paul Scherrer Institute, Villigen PSI CH-5232, Switzerland; orcid.org/0000-0001-8624-2649

Alex Comas-Vives — Department of Chemistry and Applied Biosciences, ETH Zürich, CH-8093, Switzerland; orcid.org/0000-0002-7002-1582

Christophe Copéret — Department of Chemistry and Applied Biosciences, ETH Zürich, CH-8093, Switzerland; orcid.org/0000-0001-9660-3890

Aaron M. Lindenburg — Department of Materials Science and Engineering, Stanford University, Stanford, California 94305, United States; Institute for Materials and Energy Sciences, SLAC National Accelerator Laboratory, Menlo Park, California 94025, United States; orcid.org/0000-0003-3233-7161

Vanessa Wood — Department of Information Technology and Electrical Engineering, ETH Zürich, Zürich CH-8092, Switzerland; orcid.org/0000-0001-6435-0227

Complete contact information is available at: https://pubs.acs.org/10.1021/acscentsci.0c00587

Author Contributions

F.K., M.A., and B.B.M. synthesized most CsPbX₃ materials. L.P. recorded halide NMR spectra. L.P., M.A., M.M., and L.K. synthesized CsPbBr₃ crystals. T.S. recorded NQR experiments. L.P., M.A., C.P., M.M., and L.K. analyzed NMR and NQR data. V.M. and A.C.-V. performed DFT calculations. N.Y. performed ab initio MD calculations. M.V.K., R.V., A.M.L., C.C., and V.W. supervised the work. L.P. and M.V.K. wrote the manuscript with input from all authors.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

M.V.K. acknowledges financial support from the European Union through the FP7 (ERC Starting Grant NANOSOLID, grant agreement [306733]) and through Horizon 2020 (ERC Consolidator Grant SCALE-HALO, grant agreement [819740]). L.P. acknowledges financial support from the Scholarship Fund of the Swiss Chemical Industry (SSCI Award 2015) and from the Swiss National Science Foundation (Early Postdoc. Mobility fellowship P2EZP2_188002). N.Y. acknowledges support from the Swiss National Science Foundation through the NCCR “Quantum Sciences and Technology” and the Swiss National Supercomputing Centre (CSCS; project IDs s831, s932). A. M. L. acknowledges support from the Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division, under Contract DE-AC02-76F00015. L. K. and T.S. acknowledge partial support from Swiss National Science Foundation (Grant 200021_169455). A.C.-V. thanks the “Ramon y Cajal” Fellowship (RyC-2016-19930) and the Spanish “Ministerio de Ciencia, Innovación y Universidades” (PGC2018-108818-A-100) for financial support. D. N. Dirin, A. Swarckar, and D. Guggisberg are acknowledged for providing samples. Frank Krumiech is acknowledged for taking HAADF-STEM pictures.

REFERENCES

(1) Kim, H.-S.; Lee, C.-R.; Im, J.-H.; Lee, K.-B.; Moehl, T.; Marchioro, A.; Moon, S.-J.; Humphry-Baker, R.; Yum, J.-H.; Moser, J. E.; Grätzel, M.; Park, N.-G. Lead iodide perovskite sensitized all-solid-state submicron thin film mesoscopic solar cell with efficiency exceeding 9%. Sci. Rep. 2012, 2 (1), 591.

(2) Lee, M. M.; Teuscher, J.; Miyasaka, T.; Murakami, T. N.; Snaith, H. J. Efficient hybrid solar cells based on meso-superstructured organohalide perovskites. Science 2012, 338 (6107), 643–647.

(3) NREL. Best research-cell efficiencies. https://www.nrel.gov/pv/assets/nl/pdfs/best-research-cell-efficiencies.20200311.pdf (accessed on March 11, 2020).

(4) Wang, Q.; Wang, X.; Yang, Z.; Zhou, N.; Deng, Y.; Zhao, J.; Xiao, X.; Rudd, P.; Moran, A.; Yan, Y.; Huang, J. Efficient blue perovskite light-emitting diodes via photoluminescence enhancement. Nat. Commun. 2019, 10 (1), 5633.

(5) Wei, H.; Huang, J. Halide lead perovskites for ionizing radiation detection. Nat. Commun. 2019, 10 (1), 1066.

(6) Zhao, X.; Ng, J. D. A.; Friend, R. H.; Tan, Z.-K. Opportunities and challenges in perovskite light-emitting devices. ACS Photonics 2018, 5 (10), 3866–3875.

(7) Utrat, H.; Sun, W.; Kaplan, A. E. K.; Krieg, F.; Ginterseder, M.; Spokony, B.; Klein, N. D.; Shulenberger, K. E.; Parkinson, C. F.; Kovalenko, M. V.; Bavendi, M. G. Coherent single-photon emission from colloidal lead halide perovskite quantum dots. Science 2019, 363 (6431), 1068–1072.

(8) 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.

(9) Zhao, Q.; Hazarika, A.; Chen, X.; Harvey, S. P.; Larson, B. W.; Teeter, G. R.; Liu, J.; Song, T.; Xiao, C.; Shaw, L.; Zhang, M.; Li, G.; Beard, M. C.; Luther, J. M. High efficiency perovskite quantum dot solar cells with charge separating heterostructure. Nat. Commun. 2019, 10 (1), 2842.

(10) Zhang, J.; Hodes, G.; Jin, Z.; Liu, S. All-Inorganic CsPbX₃ perovskite solar cells: Progress and prospects. Angew. Chem., Int. Ed. 2019, 58, 15596–15618.

(11) Kim, Y. C.; Kim, K. H.; Son, D.-Y.; Jeong, D.-N.; Seo, J.-Y.; Choi, Y. S.; Han, I. T.; Lee, S. Y.; Park, N.-G. Printable organometal halide perovskites. Adv. Energy Mater. 2017, 7 (19), 1700600.

(12) He, Y.; Matei, L.; Jung, H. J.; McCall, K. M.; Chen, M.; Stoumpos, C. C.; Liu, Z.; Peters, J. A.; Chung, D. Y.; Wessels, B. W.; Wasielewski, M. R.; Dravid, V. P.; Burger, A.; Kanatzidis, M. G. High spectral resolution of gamma-rays at room temperature by perovskite CsPbBr₃ single crystals. Nat. Commun. 2018, 9 (1), 1609.

(13) Wei, H.; DeSantis, D.; Wei, W.; Deng, Y.; Guo, D.; Savenije, T. J.; Cao, L.; Huang, J. Dopant compensation in alloyed CH₃NH₃PbBr₃–CL perovskite single crystals for gamma-ray spectroscopy. Nat. Mater. 2017, 16, 826–833.

(14) Anusca, I.; Balčiunas, S.; Gemeiner, P.; Svivskas, Š.; Šalčiulis, M.; Lackner, G.; Fettkenhauer, C.; Belovickis, J.; Samulionis, V.; Ivanov, M.; Dkhil, B.; Banyš, J.; Shvartsman, V. V.; Lupascu, D. C. Dielectric response: answer to many questions in the methylammonium lead halide solar cell absorbers. Adv. Energy Mater. 2017, 7 (19), 1700600.

(15) Miyata, K.; Atallah, T. L.; Zhu, X.-Y. Lead halide perovskites: Crystal-liquid duality, phonon glass electron crystals, and large polaron formation. Sci. Adv. 2017, 3 (10), No. e1701469.

(16) Guo, Y.; Yaffe, O.; Hall, T. D.; Owen, J. S.; Reichman, D. R.; Brus, L. E. Dynamic emission Stokes shift and liquid-like dielectric solvent of band edge carriers in lead-halide perovskites. Nat. Commun. 2019, 10 (1), 1175.

(17) Chu, W.; Zheng, Q.; Prezhold, O. V.; Zhao, J.; Saidi, W. A. Low-frequency lattice phonons in halide perovskites explain high defect tolerance toward electron-hole recombination. Sci. Adv. 2020, 6 (7), No. eaaw7453.
(18) Gehrmann, C.; Egger, D. A. Dynamic shortening of disorder potentials in anharmonic halide perovskites. Nat. Commun. 2019, 10 (1), 3141.
(19) Massiot, D.; Messinger, R. J.; Cadars, S.; Deschamps, M.; Montouillout, V.; Pellerin, N.; Veron, E.; Allix, M.; Florian, P.; Fayon, F. Topological, geometric, and chemical order in materials: insights from solid-state NMR. Acc. Chem. Res. 2013, 46 (9), 1975–1984.
(20) Moran, R. P.; Dawson, D. M.; Ashbrook, S. E. Exploiting NMR spectroscopy for the study of disorder in solids. Int. Rev. Phys. Chem. 2017, 36 (1), 39–115.
(21) Kubicki, D. J.; Prochowicz, D.; Hofstetter, A.; Zakeeruddin, S. M.; Grätzel, M.; Emsley, L. Phase segregation in potassium-doped lead halide perovskites from 39K solid-state NMR at 21.1 T. J. Am. Chem. Soc. 2018, 140 (23), 7232–7238.
(22) Kubicki, D. J.; Prochowicz, D.; Hofstetter, A.; Zakeeruddin, S. M.; Grätzel, M.; Emsley, L. Phase segregation in Cs-, Rb- and K-dope mixed-Cation (MA)x(FA)1-xPbI3 hybrid perovskites from solid-state NMR. J. Am. Chem. Soc. 2017, 139 (40), 14173–14180.
(23) Prochowicz, D.; Yadav, P.; Saliba, M.; Kubicki, D. J.; Tavakoli, M. M.; Zakeeruddin, S. M.; Lewin, J. C.; Gautier, R.; Bataille, T.; Deleporte, E.; Even, J.; Katan, C. Multinuclear NMR as a tool for studying local order and potential optoelectronic materials showing bright emission with wide color gamut. Nano Lett. 2015, 15 (6), 3692–3696.
(24) Yazdani, N.; Nguyen-Thanh, T.; Yarem, M.; Lim, W. M. M.; Gao, R.; Yarem, O.; Bosak, A.; Wood, V. Measuring the vibrational density of states of nanocrystal-based thin films with inelastic X-ray scattering. J. Phys. Chem. Lett. 2018, 9 (7), 1561–1567.
(25) Yaffe, O.; Guo, Y.; Tan, L. Z.; Egger, D. A.; Hull, T.; Stoumpos, C. C.; Zheng, F.; Heinz, T. F.; Kronik, L.; Kanatzidis, M. G.; Owen, J. S.; Rappé, A. M.; Pimenta, M. A.; Brus, L. E. Local polar fluctuations in lead halide perovskite crystals. Phys. Rev. Lett. 2017, 118 (13), 136001.
(26) Zhao, X.; Dalpian, G. M.; Wang, Z.; Zunger, A. The polymorphous nature of cubic halide perovskites. arXiv e-prints, 2019, arXiv:1905.09141. https://arxiv.org/abs/1905.09141.
(27) Akkerman, Q. A.; Rainó, G.; Kovalenko, M. V.; Manna, L. Genesis, challenges and opportunities for colloid lead halide perovskite nanocrystals. Nat. Mater. 2018, 17 (5), 394–405.
(28) Kovalenko, M. V.; Protesescu, L.; Bodnarchuk, M. I. Properties and potential optoelectronic applications of lead halide perovskite nanocrystals. Science 2017, 358 (6364), 745–750.
(29) Krieg, F.; Ochsehnein, S. T.; Yakunin, S.; ten Brinck, S.; Aellen, P.; Siess, A.; Clerc, B.; Guggisberg, D.; Nazarenko, O.; Shynkarenko, Y.; Kumar, S.; Shih, C.-J.; Infante, I.; Kovalenko, M. V. Colloidal CsPbX3 (X = Cl, Br, I) nanocrystals 2.0: Zwitterionic capping ligands for improved durability and stability. ACS Energy Lett. 2018, 3 (3), 641–646.
(30) Fujiy, J.; Hoshino, S.; Yamada, Y.; Shirane, G. Neutron-scattering study on phase transitions of CsPbCl3. Phys. Rev. B 1974, 9 (10), 4549–4559.
(31) Le Caër, G.; Bureau, B.; Massiot, D. An extension of the Cžekż model for the distributions of electric field gradients in disordered solids and an application to NMR spectra of 71Ga in chalcogenide glasses. J. Phys.: Condens. Matter 2010, 22 (6), 065402.
(32) Maurer, M. Electric field gradients of randomly disordered compounds. Phys. Rev. B: Condens. Matter Mater. Phys. 1986, 34 (12), 8996–8999.
(33) Slenezyova, K.; Sergeev, N. A.; Olszewski, M.; Stepien, P.; Yagupov, S. V.; Strugatsky, M. B.; Kliava, J. Fitting MAS NMR spectra in crystals with local disorder: Cžekż’s vs. Maurer’s model for 11B and 71Ga in polycrystalline gallium borate. Solid State Nucl. Magn. Reson. 2017, 10061, 85–86, 12–18.
(34) Chabin, M.; Gilletta, F. Experiment investigation of the ferroelastic domain structure in cesium lead chloride in the monoclinic phase. J. Appl. Crystallogr. 1980, 13 (6), 539–543.
(35) Shin, E. J.; Jeong, H. K.; Kim, S. Y.; Jeong, J. The orientation of ferroelastic domain in single crystal, CsPbCl3. J. Korean Assoc. Cryst. Growth 1997, 7 (1), 117–125.
(56) Jeong, H. T.; Cho, Y. C.; Cho, C. R.; Jeong, S.-Y. Consideration on domain walls orientations in CsPbCl₃ ferroelastic crystal in the monoclinic phase. J. Phys. Soc. Jpn. 2001, 70 (3), 717−722.

(57) Walsh, A.; Stranks, S. D. Taking control of ion transport in halide perovskite solar cells. ACS Energy Lett. 2018, 3 (8), 1983−1990.

(58) Maier, J. Nanoionics: Ion transport and electrochemical storage in confined systems. Nat. Mater. 2005, 4 (11), 805−815.

(59) Azpuru, J. M.; Mosconi, E.; Bisquert, J.; De Angelis, F. Defect migration in methylammonium lead iodide and its role in perovskite solar cell operation. Energy Environ. Sci. 2015, 8 (7), 2118−2127.

(60) Mosconi, E.; De Angelis, F. Mobile Ions in organohalide perovskites: Interplay of electronic structure and dynamics. ACS Energy Lett. 2016, 1 (1), 182−188.

(61) ten Brinck, S.; Infante, I. Surface termination, morphology, and bright photoluminescence of cesium lead halide perovskite nanocrystals. ACS Energy Lett. 2016, 1 (6), 1266−1272.

(62) Venkataraman, G. Soft modes and structural phase transitions. Bull. Mater. Sci. 1979, 1 (3), 129−170.

(63) Hirotsu, S. Structural Studies of Experimental Structural Phase Transitions in CsPbCl₃. J. Phys. Soc. Jpn. 1971, 31 (2), 552−560.

(64) Beecher, A. N.; Seminon, O. E.; Skelton, J. M.; Frost, J. M.; Terban, M. W.; Zhai, H.; Alatas, A.; Owen, J. S.; Walsh, A.; Billinge, S. J. L. Direct observation of dynamic symmetry breaking above room temperature in methylammonium lead iodide perovskite. ACS Energy Lett. 2016, 1 (4), 880−887.

(65) Whalley, L. D.; Skelton, J. M.; Frost, J. M.; Walsh, A. Phonon anharmonicity, lifetimes, and thermal transport in CH₃NH₃PbI₃ from many-body perturbation theory. Phys. Rev. B: Condens. Matter Mater. Phys. 2016, 94 (22), 220301.

(66) Marronnier, A.; Roma, G.; Boyer-Richard, S.; Pedesseau, L.; Jancu, J.-M.; Bonnassieux, A.; Cervellino, A.; Billinge, S. J. L.; Terban, M. W.; Zhai, H.; Alatas, A.; Owen, J. S.; Walsh, A.; Billinge, S. J. L. Defect migration in methylammonium lead iodide and its role in perovskite solar cell operation. Energy Environ. Sci. 2015, 8 (7), 2118−2127.

(67) Marronnier, A.; Lee, H.; Geffroy, B.; Even, J.; Bonnassieux, Y.; Roma, G. Structural instabilities related to highly anharmonic phonons in halide perovskites. J. Phys. Chem. Lett. 2017, 8 (12), 2659−2665.

(68) Volkov, A. F.; Veniutsev, Y. N.; Semin, G. K. Nuclear quadrupole resonance (NQR) of ⁷⁹Br and ⁸¹Br in perovskite and orthorhombic forms of CsPbBr₃ and CsPbI₂. Phys. Status Solidi B 1969, 35 (2), K167−K169.

(69) Sharma, S.; Weiden, N.; Weiss, A. Phase transitions in CaSnCl₄ and CaSnBr₄, an NMR and NQR study. Z. Naturforsch., A: Phys. Sci. 1991, 46 (4), 329−336.

(70) Xu, Q.; Eguchi, T.; Nakayama, H.; Nakamura, N.; Kishita, M. Molecular motions and phase transitions in solid CH₃NH₃PbX₃ (X = Cl, Br, I) as studied by NMR and NQR. Z. Naturforsch., A: Phys. Sci. 1991, 46, 240−246.

(71) Bertolotti, F.; Protescu, L.; Kovalenko, M. V.; Yakunin, S.; Cervellino, A.; Billinge, S. J. L.; Terban, M. W.; Pedersen, J. S.; Masiocchi, N.; Guagliardi, A. Coherent nanotwins and dynamic disorder in cesium lead halide perovskite nanocrystals. ACS Nano 2017, 11 (4), 3819−3831.

(72) Das, T. P.; Hahn, E. L. Nuclear Quadrupole Resonance Spectroscopy; Academic Press Inc.: London, 1958.

(73) Harris, R. K.; Becker, E. D.; Cabral de Menezes, S. M.; Goodfellow, R.; Granger, P. Nuclear spin properties and conventions for chemical shifts. Pure Appl. Chem. 2001, 73 (11), 1795−1818.

(74) Stoumpos, C. C.; Malliakas, C. D.; Kanatzidis, M. G. Semiconducting tin and lead iodide perovskites with organic cations: Phase transitions, high mobilities, and near-infrared photoluminescent properties. Inorg. Chem. 2013, 52 (15), 9019−9038.

(75) Sutton, R. J.; Filip, M. R.; Haghighirad, A. A.; Sakai, N.; Wenger, B.; Giustino, F.; Snaith, H. J. Cubic or Orthorhombic? Revealing the Crystal Structure of Metastable Black-Phase CsPbI₃ by Theory and Experiment. ACS Energy Letters 2018, 3 (8), 1787−1794.