Lead-Halide Scalar Couplings in $^{207}$Pb NMR of APbX$_3$ Perovskites (A = Cs, Methylammonium, Formamidinium; X = Cl, Br, I)

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Understanding the structure and dynamics of newcomer optoelectronic materials - lead halide perovskites APbX$_3$ (A = Cs, methylammonium (CH$_3$NH$_3^+$, MA), formamidinium (CH(NH$_2$)$_2^+$, FA); X = Cl, Br, I) - has been a major research thrust. In this work, new insights could be gained by using $^{207}$Pb solid-state nuclear magnetic resonance (NMR) spectroscopy at variable temperatures between 100 and 300 K. The existence of scalar couplings $^1$J$_{Pb-Cl}$ of ca. 0.4 kHz and $^1$J$_{Pb-Br}$ of ca. 2.3 kHz could be confirmed for MAPbX$_3$ and CsPbX$_3$. Diverse and fast structure dynamics, including rotations of A-cations, harmonic and anharmonic vibrations of the lead-halide framework and ionic mobility, affect the resolution of the coupling pattern. $^{207}$Pb NMR can therefore be used to detect the structural disorder and phase transitions. Furthermore, by comparing bulk and nanocrystalline CsPbBr$_3$ a greater structural disorder of the PbBr$_6$-octahedra had been confirmed in a nanoscale counterpart, not readily captured by diffraction-based techniques.

Semiconducting lead halide perovskite materials, foremost of APbX$_3$-type (A = Cs, methylammonium (CH$_3$NH$_3^+$, MA), formamidinium (CH(NH$_2$)$_2^+$, FA); X = Cl, Br, I), have raised tremendous interest over the past years due to their outstanding optoelectronic properties, which find application in solar cells$^{1,2}$, X-ray$^3$ and gamma detectors$^4$–$^6$ and light-emitting devices$^7$–$^{14}$. These semiconductors exhibit unusually high defect-tolerance, which is the nearly intrinsic semiconducting behaviour in spite of the high abundance of structural imperfections. Such defect-tolerance had been attributed to the specifics of the electronic structure, crystal structure and structural dynamics$^{15}$–$^{21}$. It is therefore fundamental to develop an experimental toolset and a related mind-set for studying the local structure and structural dynamics as well as their relationship to the electronic and physical properties of these semiconductors. Solid-state nuclear magnetic resonance (NMR) is a powerful technique for characterizing solid materials. It is complementary to X-ray diffraction, as it is particularly sensitive to the local environment of nuclei. Chemical composition of APbX$_3$ makes these compounds very well suited for NMR, owing to the range of NMR-active nuclei (1H$^{22}$–$^{25}$, 2H$^{22}$,23,26–$^{28}$, 13C$^{22}$–$^{25}$,29, 14N$^{22}$–$^{27}$,29, 15N$^{25}$,30, 133Cs$^{29}$,31, 207Pb$^{23}$–$^{25}$,27,31–$^{33}$, 35Cl, 37Cl, 79Br, 81Br, 127I)$^{34}$. In this contribution, we focus on $^{207}$Pb NMR spectroscopy of APbX$_3$ compounds and report on the existence of scalar lead-halide J-couplings in some of them. $^1$J$_{Pb-Cl}$ of ca. 400 Hz and $^1$J$_{Pb-Br}$ of ca. 2.5 kHz have been measured for MAPbX$_3$ and CsPbX$_3$ compounds. For other compounds within the APbX$_3$ family, scalar couplings are elucidated to be on the order of 2–3 kHz but had not been spectrally resolved. The temperature dependence of the couplings correlates with the known reduction of the structural dynamics and ionic mobility in these perovskites$^{35}$. In APbX$_3$ perovskite compounds, corner-sharing lead-halide octahedra form a 3-dimensional (3D) anionic network, charge-stabilized by A-cations filling large 12-fold-coordinated voids in-between the octahedra. Several 3D-polymorphs of these compounds exist, but they differ in the distortion of the lead-halide octahedral lattice (Fig. 1a; see Table S1 for a detailed overview of known structures at various temperatures). This structural data is correlated in the following discussion with our NMR data. The compounds consist of a dynamic inorganic
PbX-framework with a high concentration of point defects (higher than 0.4% in MAPbI3 at room temperature\(^3\)) leading to defect-mediated hopping of the halide anions\(^3\). These frameworks are coupled through ion-ion interactions and hydrogen bonds to the A-cation. The rotation and displacement of the A-cations lead to distortions and anharmonic vibrations in the whole perovskite structures\(^3\), which has been shown by Whalley et al.\(^3\), Beecher et al.\(^4\) for MAPbI3 and by Marronnier et al.\(^4\),\(^5\) for CsPbI3. All these dynamic processes take place in the picosecond time scale and contribute to the soft structure of the lead halide perovskites. They can be diminished or for some rotations even completely suppressed by reducing the temperature.

NMR studies on lead halide perovskites had already been launched in the 1980s. For MAPbX\(_3\), Wasylishen reported in 1985 on the dynamics of the organic cation and phase transitions using \(^2\)H and \(^14\)N NMR\(^2\). Most of the subsequent studies concentrated on \(^1\)H, \(^2\)H, \(^1\)C, \(^14\)N, \(^1\)N nuclei to characterize and understand the dynamics and mobility of the organic cations (MA or FA)\(^2\),\(^3\),\(^4\),\(^5\). Only a few studies concerned \(^1\)Cs NMR\(^5\),\(^6\),\(^7\),\(^8\),\(^9\),\(^10\) as to the halides, NMR spectroscopy had thus far been hampered by their large quadrupolar constants, leading to massively broadened signals and distorted line shapes\(^10\),\(^11\). For this reason, halides are more commonly assessed with nuclear quadrupole resonance (NQR) spectroscopy\(^12\),\(^13\),\(^14\),\(^15\),\(^16\),\(^17\). Sharma et al.\(^18\) (1987) and the dissertation by Ullmann (1998)\(^19\) are, to our knowledge, the first reports on \(^2\)Pb NMR of lead-halide perovskites. Two decades later, \(^2\)Pb NMR studies had been resumed by Rosales et al.\(^20\), who studied mixed-halide methylammonium perovskites. The last three years have seen the increasing use of \(^2\)Pb NMR for the characterization of APbX\(_3\), perovskites and novel lead halide compounds\(^2\),\(^3\),\(^4\),\(^5\),\(^6\),\(^7\),\(^8\),\(^9\). In these studies, MAPbI3 has been the main focus. It was studied at variable temperatures\(^2\),\(^3\),\(^4\),\(^5\),\(^6\),\(^7\),\(^8\),\(^9\), during decomposition\(^6\), with dimethylammonium incorporation\(^6\) and also with bromine substitution\(^2\). 2D NMR and dynamic nuclear polarization (DNP) NMR was measured for micro- and nanocrystalline MAPbX\(_3\) at 100 K, which resulted in an enhancement factor of up to 20 for MAPbCl\(_3\)\(^6\),\(^7\). MAPbCl\(_3\) was additionally measured at various temperatures and its utility as an internal thermometer was shown based on the temperature dependence of its \(^2\)Pb NMR chemical shift\(^6\).

Results and Discussion
Of fundamental importance are the first observations of lead-halide J-coupling in MAPbCl\(_3\) (\(^{\text{1}^\text{JPb-Cl}}\)) and in CsPbBr\(_3\) as well as Cs\(_3\)PbBr\(_7\).\(^3\),\(^7\). J-couplings are mediated through bonds by hyperfine interactions between the nuclei and their local electrons. The J-coupling contains information about bond length and angles. It resonates.
with the notion that the Pb-halide framework in APbX$_3$ compounds exhibits substantial covalency and directionality in the Pb-X bonding, which is needed for efficient through-bond J-coupling. The existence of these bonds has recently been verified with band structure calculations by Goesten and Hoffmann.

Lead-halide J-couplings had already been postulated by Dybowski et al. for PbI$_3$ (built from face-sharing Pb-I octahedra), but could not be resolved. For the $^{207}$Pb NMR signal with a full-width at half-maximum (FWHM) of 20 kHz, they calculated a scalar coupling $^1$J$_{Pb-Cl}$ of 4.9 kHz, which is of a similar magnitude as other scalar couplings involving $^{207}$Pb.

The observation of J-coupling depends on several factors such as nuclear spin and quadrupolar moment of the halide as well as any dynamic changes in the structure or structural defects. The nuclear spin of the halide determines the number of lines present within the coupling pattern, while the large quadrupolar constant of the halides generally broadens the signal and therefore masks the J-coupling. The next factor that affects the observation of J-coupling is a combined effect of structural inhomogeneities that are primarily due to structural dynamics but also to static structural defects. A distribution of chemical sites, which can be caused, for instance, by vacancies or doping, leads to (inhomogeneous) broadening of the lines. Structure dynamics of the lead halide sublattice falls in the picosecond range, which is too fast for the NMR time scale (µs-to-seconds) and will be averaged out and seen as a quasi-static impact on the observed NMR spectrum. The major type of Pb-halide atomic motion is the tilting of the lead-halide octahedra with respect to each other. This constantly changes the Pb-X-Pb bond angle and therefore affects the orbital overlap thus obscuring the J-coupling. We therefore expect that the J-coupling is a sensitive probe for the structural dynamics or disorder. This disorder was also related to the phonon anharmonicity observed in hybrid perovskites. It is also important to note that the dynamic disorder of the A-site cation is correlated to that of the Pb-halide framework. Differences in the Pb-X bond length will result in slightly unequal coupling strengths to the individual halides in the lattice. A perfect PbX$_6$-octahedron should therefore yield narrower lines compared to a distorted one. This has been shown on $^{207}$Pb-$^{13}$F couplings in amorphous Pb$_x$Ga$_{1-x}$F$_3$. J-couplings to quadrupolar nuclei are known to be self-decoupled, due to their fast relaxation induced by the quadrupole. The fact that in these perovskite materials the couplings are clearly visible, indicates a relatively slow quadrupolar relaxation of the halides. Once observed, the J-coupling could be, in principle, correlated to the atomic structure. While calculations of J-couplings are sufficiently accurate for light elements, yet for lead-halide perovskites, it is needed to start drawing correlations with the structural motives (bond length/angles, corner/edgeface-sharing connectivity, octahedral or other lead halide building blocks etc.).

All studied APbX$_3$ compounds were synthesized using solution-phase methods, as reported earlier (see Supporting Information for synthesis details). We note that the as-synthesized 3D-polymorph of FAPbI$_3$ (α-phase) rapidly converts into a face-sharing 1D-polymorph (β-phase) under magic angle spinning (MAS) NMR and therefore we could acquire the spectrum only under static conditions (Fig. S1). For CsPbI$_3$, only the 1D-phase (β-phase) with edge-sharing octahedra is stable at RT, the hypothesis that an underlying scalar coupling is responsible for the observed overall spectral width is plausible. The absence of visible lines in the multiplet in MAPbBr$_3$ can be explained by the greater broadening of the individual lines. Potential interactions causing such line-broadening in NMR are the dipolar coupling, the chemical shift anisotropy (CSA), site disorder, structural dynamics, and fast relaxation. Since the sample is spun at the magic angle at 10 kHz or faster, dipolar couplings (80–280 Hz for Pb-X, and 25 Hz for Pb-Cs and Pb-Pb) and CSAs are averaged out. In a reference experiment, under static conditions, these two interactions etc are needed to start drawing correlations with the structural motives (bond length/angles, corner/edge-face-sharing connectivity, octahedral or other lead halide building blocks etc.).

RT MAS solid-state $^{207}$Pb NMR spectra of powdered Cs and MA compounds are displayed in Fig. 1b. In agreement with the earlier reports, no scalar couplings were found neither for MAPbI$_3$ (blue left, Fig. 1b) nor for MAPbBr$_3$ (blue middle, Fig. 1b). δ-CsPbI$_3$ showed no scalar coupling either (red left, Fig. 1b). However, chloride compounds exhibit pronounced J-couplings of $^1$J$_{Pb-Cl}$ = 400 Hz in CsPbCl$_3$ (red right, Fig. 1b) and $^1$J$_{Pb-Br}$ = 390 Hz in MAPbCl$_3$ (blue right, Fig. 1b). The latter is similar to that reported by Bernard et al. The similar strong scalar coupling was observed for CsPbBr$_3$, $^1$J$_{Pb-Br}$ = 2.3 kHz (red middle, Fig. 1b). This shows that Pb-Br scalar couplings are possible and that the $^{207}$Pb NMR spectra of CsPbBr$_3$ and CsPbBr$_3$ acquired and presented in the dissertation of Ullmann appear to exhibit coupling patterns as well although not named and rationalized as such by the author. The coupling patterns observed for CsPbBr$_3$ as well as for CsPbCl$_3$ and MAPbCl$_3$ (Fig. S2) can be safely attributed to scalar coupling since the splitting between the lines stays unchanged at different magnetic fields but changes with temperature (Fig. 2).

The coupling pattern matches expectations for lead coordinated to six equivalent halides in an octahedron. Under 1st order conditions, the signal of a nucleus coupled with n magnetically equivalent nuclei of spin I is a multiplet with 2n + 1 lines. Accordingly, for six equivalent halides (n = 6) with spin I = 7/2, the multiplet has 19 lines. PbPb-CsA a multiplet with 19 lines is anticipated. The intensity of the individual lines is obtained by constructing a coupling pattern for a spin I = 7/2, related to Pascal’s triangle. The coupling pattern of CsPbCl$_3$ and MAPbBr$_3$, at 100 K were simulated by using the experimental scalar couplings of 2.5 and 2.35 kHz, the theoretical intensities from the coupling tree to six equivalent spins I = 7/2, related to Pascal's triangle. The coupling pattern of CsPbBr$_3$, and MAPbBr$_3$ acquired and presented in the dissertation of Ullmann appear to exhibit coupling patterns as well although not named and rationalized as such by the author. The coupling patterns observed for CsPbBr$_3$ as well as for CsPbCl$_3$ and MAPbCl$_3$ (Fig. S2) can be safely attributed to scalar coupling since the splitting between the lines stays unchanged at different magnetic fields but changes with temperature (Fig. 2).

Based on the observation that CsPbBr$_3$ and MAPbBr$_3$ possess similar total linewidth in their $^{207}$Pb NMR spectra, the hypothesis that an underlying scalar coupling is responsible for the observed overall spectral width is plausible. The absence of visible lines in the multiplet in MAPbBr$_3$ can be explained by the greater broadening of the individual lines. Potential interactions causing such line-broadening in NMR are the dipolar coupling, the chemical shift anisotropy (CSA), site disorder, structural dynamics, and fast relaxation. Since the sample is spun at the magic angle at 10 kHz or faster, dipolar couplings (80–280 Hz for Pb-X, and 25 Hz for Pb-Cs and Pb-Pb) and CSAs are averaged out. In a reference experiment, under static conditions, these two interactions etc are needed to start drawing correlations with the structural motives (bond length/angles, corner/edge-face-sharing connectivity, octahedral or other lead halide building blocks etc.).

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Structural disorder, especially of a dynamic nature, is strongly dependent on temperature in the mobile lead halide lattices as is evidenced by the NMR experiments at low temperatures (Figs. 2 and 3). The low-temperature measurements in this study were carried out at 100 K, since at this temperature all lead halide perovskites are reported to be in their lowest-temperature polymorph. No further phase-transitions were reported to occur below 100 K.

The isotropic chemical shift of all compounds substantially changes towards higher frequencies upon cooling, which is typical for the $^{207}$Pb NMR signal. For CsPbBr$_3$, one can clearly observe an improved resolution of the coupling pattern at 100 K (Fig. 3). The FWHM of the individual lines narrows from 2.7 to 2.1 kHz while the coupling strength increases from 2.3 to 2.5 kHz. The stronger coupling can be explained by the contraction of the unit cell that occurs upon cooling leading to a shortening of the Pb-Br bonds$^{86-88}$. A more prominent improvement of the coupling resolution can be observed for MAPbBr$_3$. After the phase transition to the orthorhombic phase below 150 K the coupling pattern appears (Figs. 3 and S4). In this phase, the motion of the MA-cation is limited to rotation around its C-N axis. This has been shown by Wasylishen et al.$^{26}$ with $^2$H and $^{14}$N NMR, by Zhu et al.$^{35}$ where the time-resolved

![Figure 2](image_url)

**Figure 2.** (a) $^{207}$Pb NMR spectra of CsPbBr$_3$ acquired at 14.1 T at 100 K (dark blue), 16.4 T at RT (black), 14.1 T at RT (light blue) at 11.7 T and RT (red). The grey lines serve as a guide to the eye by marking the lines of the coupling pattern. The spectra are displayed against a frequency axis centered around 0 Hz. This illustrates most clearly the constant splitting distance (in Hz) between lines, due to a scalar coupling of $^{1}J_{Pb-Br} = 2.3$ kHz at RT. (b) Coupling trees for six equivalent spins $I = \frac{3}{2}$ (top) and the $^{207}$Pb NMR spectra of CsPbBr$_3$ (left) and MAPbBr$_3$ (right) acquired at 100 K on a 14.1 T instrument. The acquired spectra are shown in black. The simulated individual lines with intensities obtained from the coupling trees and scalar couplings of 2.5 and 2.4 kHz for CsPbBr$_3$ and MAPbBr$_3$, respectively, are displayed in light blue. The sum of the lines is shown in dark blue and is matching the experimental data.

![Figure 3](image_url)

**Figure 3.** $^{207}$Pb NMR spectra of CsPbBr$_3$ (left), MAPbBr$_3$ (middle) and FAPbBr$_3$ (right). The spectra acquired at RT are shown in red (top) and the ones at 100 K in blue (bottom). The isotropic chemical shifts and the coupling constants are listed in Table 1. A possible coupling in FAPbBr$_3$ is difficult to observe due to the low signal-to-noise ratio.
All isotopes of chlorine and bromine have a spin of $I = \frac{5}{2}$ and a quadrupole moment more than twice as large as the bromine. Possible Pb-I couplings were calculated by Bernard et al. in MAPbI$_3$ to be around 4.9 kHz and by Bernard et al. in MAPbI$_3$ to be between 2 and 3 kHz. So far, none of these couplings could be experimentally resolved.

For MAPbI$_3$, low activation energy for migration of iodine and MA was calculated by Eames et al.$^{36}$, and confirmed by experimental studies.$^{24,39}$ This ion migration will additionally disturb the PbI$_6$-octahedra. Low-temperature measurements will, therefore, be indispensable for the resolution of Pb-I scalar couplings. At 100 K, a broad tensor was observed for APbI$_3$, which is significantly narrower than that of CsPbBr$_3$. All Pb-Br bonds are identical in Cs$_4$PbBr$_6$ and CsPbI$_3$, and this leads to a smaller coupling constant distribution that narrows the linewidth.$^{94}$ This clearly shows the effect of lattice distortions on the coupling. For a better insight into this effect, the comparison with 0D hybrid materials with MA and FA would be indispensable. Unfortunately, these materials are so far not known.

We have then also probed the effect of dimensionality by comparing bulk material and colloidal nanocrystals (NCs) of CsPbBr$_3$ (Fig. 4). These NCs have recently become an object of intense research due to their outstanding luminescent properties – narrow-band emission with high absolute quantum yields, highly suited for applications.

| Compound       | Temperature | $\delta_{iso}$ (ppm) | $^1J_{Pb,X}$ (Hz) | FWHM lines (Hz) | FWHM total (kHz) |
|----------------|-------------|----------------------|------------------|-----------------|-----------------|
| CsPbCl$_3$     | RT$^{a)}$   | −714                 | 400              | 600             | 2.4             |
| CsPbBr$_3$     | RT$^{a)}$   | 262                  | 2300             | 2400            | 13.8            |
|                 | 100 K$^{b)}$ | 130                  | 2500             | 2100            | 16.9            |
| CsPbBr$_3$, NCs| RT$^{a)}$   | 252                  | —                | —               | 17.6            |
| CsPbI$_3$      | RT$^{a)}$   | 1100                 | —                | —               | 20.0            |
|                 | 100 K$^{b)}$ | 990                  | —                | —               | 25.0            |
| MAPbCl$_3$     | RT$^{a)}$   | −630                 | 390              | 600             | 2.3             |
| MAPbBr$_3$     | RT$^{a)}$   | 365                  | —                | —               | 13.6            |
|                 | 100 K$^{b)}$ | 125                  | 2350             | 2350            | 16.6            |
| MAPbI$_3$      | RT$^{a)}$   | 1445                 | —                | —               | 17.6            |
|                 | 100 K$^{b)}$ | 1030                 | —                | —               | 20.0            |
| FAPbBr$_3$     | RT$^{a)}$   | 515                  | —                | —               | 13.1            |
|                 | 100 K$^{b)}$ | 280                  | —                | —               | 13.4            |
| FAPbI$_3$      | RT$^{a)}$   | 1515                 | —                | —               | 22.2            |

Table 1. $^{207}$Pb NMR data of APbX$_3$ perovskites. Acquired under MAS at a) 20 kHz, b) 10 kHz. Spinning at faster MAS increases the temperature of the sample and therefore changes the chemical shift (Fig. S3).
in television displays\textsuperscript{8,21,83}. The coupling cannot be resolved at RT, and the total linewidth increases to 17.6 kHz. This is attributed to higher PbBr\textsubscript{6}-octahedral disorders over the whole nanocrystal compared to the bulk material.

**Conclusions**

In summary, scalar couplings between \(^{207}\text{Pb}\) and halide nuclei (\(^{35}\text{Cl}, ^{35}\text{Cl}, ^{79}\text{Br}, ^{81}\text{Br}\)) have been detected in \(^{207}\text{Pb}\) NMR spectra of APbX\textsubscript{3} perovskites. The coupling strengths are in the range of 400 Hz for \(^{1}\text{JPb-Cl}\) and 2.3 kHz for \(^{1}\text{JPb-Br}\). Only CsPbCl\textsubscript{3} and CsPbBr\textsubscript{3} exhibit pronounced coupling patterns at RT. The substantial diminishing of structural dynamics in MAPbBr\textsubscript{3} at temperatures below 150 K results in the resolution of the J-coupling. For the iodine compounds, a coupling \(^{1}\text{JPb-I}\) of ca. 3 kHz can only be postulated based on the overall spectral line width, but it could not be experimentally resolved. Future studies might concentrate on resolving Pb-iodide couplings at lower magnetic fields. \(^{207}\text{Pb}\) NMR has shown to be an easily accessible tool to detect permanent and dynamic distortions in the inorganic framework of perovskites. This shows its great potential to better characterize these materials, which is not possible by normal X-ray diffraction. Another important avenue is to probe the relationship between Pb-Br J-couplings and the structural disorder induced by the dimensionality, for instance, in colloidal CsPbBr\textsubscript{3} NCs.

**Methods**

APbX\textsubscript{3} (A = Cs, MA, FA; X = Cl, Br, I) compounds were synthesized in the corresponding hydrohalic acid. CsPbX\textsubscript{3} was additionally prepared from the solid state by melting together CsX and PbX\textsubscript{2} in a 1:1 ratio. CsPbBr\textsubscript{3} NCs were prepared by hot injection using long-chain zwitterionic molecules as capping ligands\textsuperscript{83}. See SI for further details. The purity of all compounds was confirmed by powder X-ray diffraction (pXRD). All samples were ground into a fine powder and densely packed into ZrO\textsubscript{2} rotors. Solid-state Magic Angle Spinning (MAS) NMR experiments at ambient conditions were performed on three Bruker Avance III HD spectrometers (Bruker Biospin, Fällanden, Switzerland). The 11.7 and 16.4 T instruments were equipped with 2.5 mm two-channel...
and three-channel solid-state probe heads. The spinning frequency was set between 0 and 20 kHz. The 14.1 T magnet was equipped with a 3.2 mm double-channel MAS probe and a MAS spinning rate of 10 kHz was used. Low-temperature experiments were conducted on the 14.1 T Bruker instrument equipped with a 3.2 mm double-channel low-temperature MAS probe using MAS chemical shifts were referenced to PbMe$_4$. A Hahn echo pulse-sequence was used for all measurements with an echo delay between 0.1 and 0.5 ms. The rf field of the echo pulses was set to 35.7, 26.3 and 19.8 kHz at 11.7, 14.1 and 16.4 T, respectively, which is strong enough to be refocused the complete spectra of the 3D phases. The 1D phases are too broad (>140 kHz) to be refocused completely.

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Author contributions
M.K. and R.V. supervised this work. M.A. and L.P. carried out NMR experiments and analyzed the results. O.N., B.B., and F.K. synthesized all samples. M.A. and M.K. wrote the manuscript with the input of all co-authors.

Competing interests
The authors declare no competing interests.

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