Revealing the Structure and Oxygen Transport at Interfaces in Complex Oxide Heterostructures via $^{17}$O NMR Spectroscopy

Michael A. Hope, Bowen Zhang, Bonan Zhu, David M. Halat, Judith L. MacManus-Driscoll, and Clare P. Grey*

ABSTRACT: Vertically aligned nanocomposite (VAN) films, comprising nanopillars of one phase embedded in a matrix of another, have shown great promise for a range of applications due to their high interfacial areas oriented perpendicular to the substrate. In particular, oxide VANs show enhanced oxide-ion conductivity in directions that are orthogonal to those found in more conventional thin-film heterostructures; however, the structure of the interfaces and its influence on conductivity remain unclear. In this work, $^{17}$O NMR spectroscopy is used to study CeO$_2$–SrTiO$_3$ VAN thin films: selective isotopic enrichment is combined with a lift-off technique to remove the substrate, facilitating detection of the $^{17}$O NMR signal from single atomic layer interfaces. By performing the isotopic enrichment at variable temperatures, the superior oxide-ion conductivity of the VAN films compared to the bulk materials is shown to arise from enhanced oxygen mobility at this interface; oxygen motion at the interface is further identified from $^{17}$O relaxometry experiments. The structure of this interface is solved by calculating the NMR parameters using density functional theory combined with random structure searching, allowing the chemistry underpinning the enhanced oxide-ion transport to be proposed. Finally, a comparison is made with 1% Gd-doped CeO$_2$–SrTiO$_3$ VAN films, for which greater NMR signal can be obtained due to paramagnetic relaxation enhancement, while the relative oxide-ion conductivities of the phases remain similar. These results highlight the information that can be obtained on interfacial structure and dynamics with solid-state NMR spectroscopy, in this and other nanostructured systems, our methodology being generally applicable to overcome sensitivity limitations in thin-film studies.

Oxide thin films exhibit an incredible variety of functional properties, which have been widely applied in electronic, magnetic, and energy devices. Oxide heterostructures combine two or more different phases, the interfaces of which induce novel or enhanced functional properties due to their unique local environments. In particular, vertically aligned nanocomposite (VAN) films, comprising nanopillars of one phase embedded in a matrix of another, have shown great promise for applications as high-temperature superconductors, ferroelectrics, multiferroics, data storage media, and electronic/ionic conductors. Unlike conventional planar multilayered heterostructures, the interfaces in VAN films are perpendicular to the substrate, resulting in significantly higher interface-to-volume ratios, more uniform strain, and control over the orthogonal transport properties, leading to their potential use in, for example, micron-sized fuel cells. A comprehensive understanding of the interfacial structures in oxide thin-film heterostructures is nevertheless required to optimize their design for these various applications, which is very experimentally challenging: the chemical composition, atomic arrangement, and electronic structure at the interfaces can be significantly different to those of the bulk, being influenced by a number of factors such as the lattice mismatch and growth conditions. Previous microscopy-based character-

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phases is dictated by the epitaxy on the STO substrate and two major types of interface can be distinguished: CeO$_2$(110)/STO(100), referred to as the 0° interface, and CeO$_2$(100)/STO(110), referred to as the 45° interface, in a ratio of ~3:1; there are also some more poorly defined, rounded, interfaces, and steps, which complicate the analysis (see Supporting Information Note 1 for quantification of the interfaces). STO has a perovskite structure ($Pm\bar{3}m$), which in the $\langle 100 \rangle$ directions comprises alternating planes with stoichiometries of SrO and TiO$_2$, respectively (Figure 1b, left), whereas in the $\langle 110 \rangle$ directions, there are alternating planes of SrTiO$_{4+}$ and O$_2^{4-}$ (Figure 1c, left). CeO$_2$, on the other hand, has a fluorite structure ($Fm\bar{3}m$): in the $\langle 100 \rangle$ directions, there are alternating planes of Ce$_{4+}$ and O$_{2-}$, and in the $\langle 110 \rangle$ directions, all of the planes have the same stoichiometry of CeO$_2$, but with an alternating Ce$_{4+}$ position (Figure 1bc, right). In both cases, the ratio of the lattice parameters (3.905 Å for STO, 5.412 Å for CeO$_2$) results in a matching of 7 STO unit cells with 5 CeO$_2$ unit cells. While such analyses can be used to determine which planes from the two materials lie parallel to each other at the interfaces, it is nontrivial to identity the local structure and composition at the interfaces and to quantify the extent of disorder/cation mixing.

Solid-state NMR is a powerful technique to study local structure and dynamics, and for oxide materials, $^{17}$O NMR in particular is extremely sensitive to local distortions caused by, e.g., surfaces, substitutional substituents, and other defects. Furthermore, oxygen motion and oxide-ion conductivity can be investigated via $^{17}$O NMR relaxometry. However, NMR and $^{17}$O NMR in particular suffer from low sensitivity; the challenge of acquiring spectra with a sufficient signal-to-noise ratio (SNR) is exacerbated when studying thin films due to the extremely low sample mass and further compounded for the study of interfaces, which, as two-dimensional (2D) entities, inherently comprise only a fraction of the sample volume. Taking these factors together, it can be seen that $^{17}$O NMR studies of interfaces in thin films are extremely challenging. There is, however, a redeeming feature: since the nanopillars are approximately 20–30 nm in diameter, the sample actually contains a comparatively large interfacial area ($\sim 10^2$ m$^{-2}$) or $\sim 1\%$ of the thin film assuming an interfacial width of 2–3 Å, consequently, these are ideal samples for the study of interfacial structure.

A further impediment to the study of thin films by NMR is the presence of the substrate, which leads to significant dilution of the sample, typically by three to five orders of magnitude. There is considerable benefit to separating the thin film from the substrate, and in this work, a lift-off procedure was therefore developed, shown in Figure S1 and described in detail in the methods, which combines the water-soluble buffer layer method of Lu et al. and the polymer-transfer layer method of Liang et al. This permits substrate-free thin films to be obtained and transferred into small volume, fast magic angle spinning (MAS), 1.3 mm outer diameter rotors.

It can be challenging to interpret the chemical shifts in NMR spectra a priori and directly derive structural information, particularly in complicated systems. Instead it has been shown to be particularly effective to combine NMR spectroscopy with density functional theory (DFT) calculations: the NMR parameters are calculated for different possible structures, which are then compared with the experimental spectra to determine which is most consistent. The parameters cannot simply be calculated, however, if the structure in

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**Figure 1.** (a) STEM image of a 20 atom % Sm-doped-CeO$_2$−STO VAN film, showing the two dominant types of interface, reproduced in part with permission from ref 30, Copyright 2019 Zhu et al., AIP publishing (http://creativecommons.org/licenses/by/4.0/). (b, c) Schematics of the orientations of the STO and CeO$_2$ structures at the two types of interface. The elements are colored as follows: O: red, Ti: blue, Sr: green, and Ce: yellow.
question is not known, such as at an interface; this hurdle can be overcome using random structure searching (RSS) or ab initio RSS (AIRSS).

In RSS, the atomic positions of some or all of the atoms in the structure are randomized, before being allowed to relax into a local low-energy arrangement; this process is repeated a sufficient number of times such that the resulting lowest-energy structures are probable candidates for the true structure(s).

Using the aforementioned lift-off procedure and selective $^{17}$O enrichment, the $^{17}$O MAS NMR spectra of the CeO$_2$–STO VAN films reveal the signal from a single anionic layer at each interface. The relative oxide-ion conductivity of the interface and bulk components is probed by varying the temperature of isotopic $^{17}$O enrichment, and NMR relaxometry is used to demonstrate the presence of motion at the interface. Furthermore, the interfacial structure is determined by comparison with the NMR parameters calculated using DFT for different possible structures derived from RSS. Overall, the NMR spectra unveil the interfacial structure and dynamics in the VAN films, and this methodology should prove generally applicable to other thin-film systems.

**RESULTS AND DISCUSSION**

**$^{17}$O NMR Spectra.** Figure 2a shows the $^{17}$O NMR spectrum of the CeO$_2$–STO VAN lift-off thin films, enriched with $^{17}$O at 450 °C. The CeO$_2$ signal, observed at 879 ppm, comprises a sharper and a broader component; the former are ascribed to bulk-like CeO$_2$ environments near the core of the nanopillars (bulk CeO$_2$ exhibits a very sharp $^{17}$O resonance at 877 ppm [32,49]) and the latter to environments nearer an interface, which are less well defined. The STO signal is observed at 466 ppm [30] and the ZrO$_2$ of the rotor can be seen at 377 ppm [51]. Between the CeO$_2$ and STO signals, a broad resonance can clearly be observed centered at 680 ppm, which is assigned to oxygen ions at the CeO$_2$–STO interface. The CeO$_2$ signal also appears to be asymmetric, corresponding to resonances at 837 ppm and approximately 1000 ppm; these are attributed to interfacial environments, which are CeO$_2$-like. Furthermore, there is some intensity at 575 ppm ascribed to STO-like interfacial environments. The inclusion of these minor signals in the deconvolution is based on the environments predicted by DFT calculations, vide infra, but was nevertheless found to improve the fits. The short recycle delay of 0.1 s somewhat suppresses the bulk signals relative to the more distorted, disordered, and/or dynamic interfacial signals, allowing the latter to be more easily observed, since the spin-lattice ($T_1$) relaxation constants of pure bulk CeO$_2$ and STO are ca. 300 and 125 s, respectively (Figures S2 and S3); the short recycle delay, however, precludes quantitative comparison of the signal intensities.

For eighteen ~1 μm thick 0.5 cm$^2$ thin films, there is a total volume of just under 1 μL, although transfer losses of around a factor of two, or greater, are expected. This corresponds to a sample mass of ~3 mg and the region of interest, i.e., the interface, constitutes only ~0.03 mg; given the extremely low active mass, it is remarkable to obtain a high-quality $^{17}$O NMR spectrum in under a day (SNR = 24). A second sample containing only four lift-off CeO$_2$–STO VAN films, rather than the eighteen used for Figure 2a, shows similar signals but took significantly longer to record (5 days, Figure S4).

**Structure of the Interface.** To interpret the spectral signatures of the VAN films, the interfaces were investigated using DFT. The major 0° interface has previously been studied in depth using RSS to find possible interfacial structures; in these calculations, the final STO layer at the interface was chosen to have the stoichiometry TiO$_2$ on the basis of STEM analysis.

As shown in Figure 1b, the planes which meet at the interface contain both metal cations and oxide anions; to avoid like-charged ions coming into close proximity, there must be significant structural rearrangement at this interface.
There is some variation of the local oxygen stoichiometry in this range. The stoichiometry of this layer, however, is not necessarily obvious: in a single supercell comprising 7 STO unit cells and 5 CeO$_2$ unit cells in the c direction, an STO anion plane contains 14 O$^{2-}$ ions and a CeO$_2$ plane contains 20 O$^{2-}$ ions; the interfacial anion layer could therefore conceivably have any stoichiometry in this range.

Initial calculations were performed on a simple model of the 45° interface (Figure 3). This model contains 14 O$^{2-}$ at the interface; in the former interface, there are too few oxygen ions to fully coordinate all of the Ce$^{4+}$ ions, so the under-coordinated cations withdraw more electron density from their adjacent oxygen anions, deshielding them and increasing the 17O shift. For the CeO$_2$-like 20 O$^{2-}$ ion interface, in the former interface; in the latter interface, the same environment in the adjacent layers, but beyond 4 Å from the interface, the 17O shifts match those of the bulk materials.

To gain further insight into the 45° interface, the same random structure searching approach previously used for the 0° interface was applied. In this case, an intermediate initial model was chosen with 17 O$^{2-}$ ions per interface; the supercell was constructed so that the two interfaces are related by a mirror plane and are therefore equivalent. Low-energy structures were found by RSS using empirical interatomic potentials, and a representative structure was relaxed with DFT (Figures 3 and S5). In this structure, there has been exchange of a Ce$^{4+}$ and a Ti$^{4+}$ ion at the interface, which was a common feature in the RSS results and suggests that cation migration (mixing) can occur at this interface to lower the interfacial energy. The 17O NMR shifts were then calculated (Figures 2c and S5); there is a wider range of shifts for the ions at the interface (670–785 ppm), with environments that are similar to both the STO- and CeO$_2$-like interfaces.

17O is a quadrupolar nucleus ($I = 5/2$), therefore in principle the quadrupolar coupling to the local electric field gradient (as measured by the quadrupolar coupling constant, $C_Q$) can provide further insight into the oxygen environments. Bulk CeO$_2$ has no 17O quadrupolar coupling ($C_Q = 0$) due to the...
tetrahedral oxygen environment and STO has a small $Q$ of 1.0 MHz; the interface, on the other hand, may be expected to have more distorted environments. Figure S8 shows the calculated $^{17}$O $Q$ constants for the two 45° interface models: the calculated $Q$ constants are low (<0.5 MHz) for the CeO$_2$ regions, increasing somewhat toward the interfaces, while the STO slabs exhibit larger $Q$ constants (~1 MHz), albeit also with a large spread. The only interface that induces markedly higher $Q$ constants is the CeO$_2$-like interface, up to 3 MHz for certain oxygen ions in the adjacent SrTiO$_4$ layer; this reflects the large anisotropy induced by having an adjacent anion from the CeO$_2$-like layer, rather than the otherwise cationic coordination. The lack of such environments in the RSS interface suggests that such high-energy environments are not realistic. However, even environments with quadrupolar coupling up to $Q = 3$ MHz would be hard to distinguish in the experimental spectrum on the basis of the second-order linewidth (~32 ppm) or shift (~20 ppm), since these are less than the experimental linewidth for the interfacial signal (115 ppm). MQMAS experiments could potentially identify such environments but would be too time consuming here due to the low SNR, and in a nutation experiment it would be challenging to differentiate the overlapping components with different quadrupolar coupling constants; therefore, in this case, further insight cannot be readily be gained from the quadrupolar coupling.

Of the models considered for the 45° interface, the best agreement with the experimental $^{17}$O NMR signal at 680 ppm is for the CeO$_2$-like interface; this may suggest an oxygen-rich stoichiometry closer to 20 O$^{2-}$ ions, which would require defects such as oxygen vacancies nearby to maintain charge neutrality. The STO-like 14 O$^{2-}$ interface is unlikely to be a major component since the calculated shifts are too high. The intermediate stoichiometry 17 O$^{2-}$ interface, however, predicts environments that are in reasonable agreement with experiment, and the structure is more realistic due to the RSS approach. A more thorough screening of the $^{17}$O shifts of other structures derived by RSS may reveal that some structures have a closer match to experiment, but this is not the aim of the present study. In any case, the 680 ppm signal can confidently be assigned to oxygen ions in the common anionic layer of the 45° interface.

The question thus arises, although this spectrum is not quantitative due to the relatively short recycle delay and possible quadrupolar nutation effects, why does there appear to be a greater intensity for environments ascribed to the 45° interface than for the 0° interface, given that TEM indicates a times three greater proportion of the latter? Since environments that resonate around 560, 840, and 990 ppm are also predicted for the 45° interface, very little of the 0° interface may actually be observed. As the $^{17}$O enrichment was performed at a reasonably low temperature (450 °C), this implies a greater oxide-ion conductivity for the 45° interface. This motivated a more detailed NMR study of the ionic transport.

Oxide-Ion Conductivity. To investigate the relative oxide-ion conductivities of the CeO$_2$, STO, and 45° interface, the $^{17}$O enrichment was performed as a function of temperature (Figure 4); the same sample and NMR rotor were progressively enriched at 250, 350, and 450 °C, without unpacking the sample, to allow direct comparison of the spectra. At the lower temperatures, there is ~5x less enrichment than at 450 °C, suggesting that there is insufficient diffusion of $^{17}$O through the thickness of the film but rather a degree of surface selectivity (in agreement with previous results on CeO$_2$ nanoparticles). Although the intensity of all of the signals increases with increasing enrichment temperature, and the recycle delay is far from quantitative, the relative oxide-ion conductivities of the phases can nevertheless be inferred from the comparative intensities. This can be more easily seen by scaling the spectra so that the interface signal has the same intensity (Figure 4b); both the CeO$_2$ and STO signals increase in intensity relative to the interface signal with increasing enrichment temperature, with a greater relative increase for the STO signal. Alternatively, by plotting the ratio of the CeO$_2$ integrated intensity to those of the interface and STO signals (Figure 4b inset), it can be seen that at higher enrichment temperatures the enrichment of the CeO$_2$ increases relative to the interface and that of the STO increases relative to the CeO$_2$. This implies that the oxide-ion conductivities are in the order: STO < CeO$_2$ < interface.

The greater mobility of the oxygen ions at the 45° interface may also be probed by relaxometry measurements. Transverse ($T_2$) decay, as measured by the change in intensity following a variable-length Hahn echo experiment, can be induced by the spins exchanging among different environments on a timescale comparable to the spread of frequencies that are sampled (see Supporting Information Note 2 for simulated exchange-induced $T_2$ decay). Since the motion of the oxygen ions will be thermally activated, the $T_2$ will be temperature-dependent if...
the motional rate is comparable to the range of frequencies sampled. Figure 5 shows the integrated intensity of the CeO$_2$ and interface signals as a function of the echo length for two different temperatures, for CeO$_2$–STO lift-off films (Figure S9), whereas the fitted $T_2$ for the interface signal is significantly shorter at the higher temperature, dropping from 1.0 ± 0.3 to 0.40 ± 0.10 ms (Table 1). A $T_2$ constant that decreases at higher temperature suggests exchange in the slow-motion regime, i.e., slower than the range of sampled frequencies. Assuming that the exchange rate follows an Arrhenius temperature dependence, and that therefore so too does the $T_2$ decay, an activation energy of 0.30 ± 0.13 eV can be estimated from the (albeit only two) temperature points. Unfortunately, the temperature limits of the low-volume fast MAS rotors prevent measurements of the $T_2$ decay at higher temperatures, so it is not possible to check whether the temperature dependence is indeed Arrhenius, but nevertheless the activation energy is consistent with previous NMR studies of oxygen motion. In any case, the temperature dependence of the $T_2$ relaxation for the $^{17}$O ions at the 45° interface provides strong evidence for oxygen motion around the kHz timescale and hence significant oxygen mobility, which would explain the greater enrichment of the 45° interface, especially at lower temperatures. The higher maximum intensity of the interface peak at 71 °C than at 41 °C, also observed in the $T_1$ measurement (Figure S7), suggests a distribution of correlation times for motion. A possible explanation is that there is a subset of environments at the interface undergoing faster exchange; these signals would coalesce at the higher temperature, increasing the peak intensity.

The high oxide-ion conductivity for the 45° interface is consistent with its poorly defined stoichiometry (Figure 3): the anionic layer can feasibly support between 14 and 20 O$^{2-}$ ions per STO–CeO$_2$ supercell, whereas charge neutrality requires 17 O$^{2-}$ ions. Both sub- or superstoichiometric oxide ions can mediate ionic transport, and the stoichiometric interface can be considered to contain three vacancies.

The oxide-ion conductivity of 20 atom % Sm-doped CeO$_2$–STO VAN films was previously reported to be two orders of magnitude higher than Sm-doped CeO$_2$ alone. Given the greater conductivity of the 45° interface observed here by variable-temperature enrichment and NMR relaxometry studies, the 45° interface may also be responsible for these results. For 25 nm pillars, assuming that the interface is 2.5 Å wide, the total interface comprises ~1% of the sample volume and the 45° interface ~0.25%. The conductivity of the 45° interface would therefore need to be four or five orders of magnitude higher than that of the bulk material to explain the observed conductivity increase. However, given the significant $^{17}$O enrichment also observed for the CeO$_2$ phase, it is likely that oxide-ion conductivity also involves the CeO$_2$ layers near the interface, possibly via migration of vacancies from the interface into the bulk and/or residual disorder and tensile strain near these interfaces; while controversial, space charge effects may also play a role.

**Gd-Doped CeO$_2$–STO Films.** A second sample of the lift-off VAN films was prepared with 1 atom % Gd-doped CeO$_2$ nanopillars in an STO matrix. Gd doping increases the oxide-ion conductivity of CeO$_2$ by introducing oxygen vacancies, and Gd-doped CeO$_2$ is a common electrolyte in solid oxide fuel cells, although typically with higher Gd concentrations of at least 10%. A further effect of Gd doping in CeO$_2$ is to reduce the $^{17}$O $T_1$ relaxation constant due to paramagnetic relaxation enhancement (PRE). To explore this effect, $T_1$ measurements were made for model bulk samples, the $T_1$ values dropping from ~550 s in pure CeO$_2$ to 0.3 s for 1 atom % Gd–CeO$_2$ (Figure S2). Thus, greater signal to noise could be achieved per unit time when measuring the Gd-doped thin films, and these experiments were performed with four 0.5 cm$^2$ films, instead of eighteen as for the undoped films. Furthermore, Gd doping affords PRE without introducing additional signals to the already crowded $^{17}$O NMR spectrum of the nanopillars because the environments directly adjacent to the Gd dopants relax too quickly to be observed (c.f. Sm- and Eu-doped CeO$_2$).

Figure 6a shows the $^{17}$O NMR spectrum of the Gd-doped CeO$_2$–STO nanopillars, enriched at 450 °C and recorded with a 0.1 s recycle delay. The spectrum is similar to the undoped films, but the CeO$_2$ signal is broader due to hyperfine coupling with the Gd dopants, so that the CeO$_2$-like interfacial resonances can no longer be resolved. The sharper component of the CeO$_2$ signal, corresponding now to environments that are far from both the interface and any Gd dopants, is

![Figure 5. $^{17}$O $T_2$ decay curves for the CeO$_2$ and interface signals measured at two different temperatures, for CeO$_2$–STO lift-off films $^{17}$O-enriched at 350 °C. The integrated intensity was measured as a function of the total echo length, $t$, in a Hahn echo experiment performed at 9.40 T and 50 kHz MAS with a 0.1 s recycle delay.](https://dx.doi.org/10.1021/acs.chemmater.0c02698)

| $T$ (°C) | CeO$_2$ | Interface |
|---------|---------|-----------|
| 41      | 1.33 ± 0.08 | 1.0 ± 0.3 |
| 71      | 1.23 ± 0.06 | 0.40 ± 0.10 |

Table 1. Fitted $T_2$ Decay Constants for the CeO$_2$ and Interface Signals at Two Different Temperatures

![Figure 6a. The $^{17}$O NMR spectrum of the Gd-doped CeO$_2$–STO nanopillars, enriched at 450 °C and recorded with a 0.1 s recycle delay. The spectrum is similar to the undoped films, but the CeO$_2$ signal is broader due to hyperfine coupling with the Gd dopants, so that the CeO$_2$-like interfacial resonances can no longer be resolved.](https://dx.doi.org/10.1021/acs.chemmater.0c02698)
The errors are estimated by the spectrum of the sample enriched at 450°C and interface signals as a function of enrichment temperature. Accordingly less intense. An additional slightly sharper component of the STO-like interface can be discerned at 250°C, as was the case for the undoped CeO2. This can also be seen by plotting the relative signal ratios as a function of the enrichment temperature (Figure 6c); again the CeO2:interface ratio increases with increasing enrichment temperature, while the CeO2:STO ratio decreases, implying that the relative conductivities are in the order: interface > CeO2 > STO. Furthermore, the ratios are comparable to the undoped case, suggesting that 1% of Gd doping has not had a significant effect on the relative conductivities, except perhaps that the oxygen mobility is greater in the CeO2 relative to the STO at 350°C, as would be expected, although there may be a large error associated with this ratio due to the broad low-intensity STO signal.

An additional experiment was also performed in which the sample was unenriched by heating in air at 250°C after having been enriched with 17O at 450°C, to induce back-exchange with 16O in the air for the more labile 17O-enriched environments. The 17O NMR spectrum (Figure 6d) exhibits a decrease in the signals of predominantly the CeO2 and interface environments, as shown by the difference spectrum. This indicates that the oxide-ion conductivity of STO is only sufficiently high at higher temperatures to allow significant exchange of 16/17O, corroborating the aforementioned higher ionic conductivity of bulk CeO2 and the interfaces, relative to STO.

CONCLUSIONS

Distinct 17O NMR signals arising from a single atomic layer at each internal solid–solid interface were observed for the first time, for the case of a thin-film oxide heterostructure formed from a CeO2–STO vertically aligned nanocomposite (VAN). This was made possible by the development of a lift-off and enrichment procedure to minimize sample loss and maximize signal to noise. The mass of thin films is already low, but as 2D entities the mass of the CeO2–STO interface is even less (∼0.01 mg for eighteen 0.5 cm² films), which represents an extreme sensitivity challenge for NMR; despite this, it was still possible to obtain high-quality 17O NMR spectra in less than a day. Doping with Gd3+ reduces the 17O T1 constants by paramagnetic relaxation enhancement, increasing the signal-to-noise ratio per unit time and allowing similar quality spectra to be obtained from fewer films.

DFT calculations then permitted the major interfacial signal to be assigned to the CeO2(100)/STO(110) “45°” interface, a potential structure for which was determined from random structure searching, consisting of an anionic layer sandwiched between Ce⁴⁺ and SrTiO⁴⁺ layers from the CeO2 and STO phases, with a stoichiometry intermediate between the two phases, with a stoichiometry intermediate between the two.
bulk structures. The qualitatively greater oxygen mobility of this interface was demonstrated by performing $^{17}$O enrichment as a function of temperature, as well as by $^{17}$O NMR relaxometry, and we propose that this specific interface makes a significant contribution to the increased oxide-ion conductivity of the CeO$_2$–STO VAN films. Enhanced oxygen mobility for this fractured interface was ascribed to the disorder and range of possible oxygen stoichiometries, which can mediate oxygen transport. By tailoring film growth to increase the proportion of the 45$^\circ$ interface, it may be possible to further improve the oxygen conductivity.

In general, new oxide heterostructures that contain shared anionic layers may have similarly enhanced oxide-ion conductivities due to the disorder and variable stoichiometry inherently imposed at the interface between two incompatible crystal structures. This is an important design principle to exploit. Furthermore, the methodology presented here will allow the atomic structure of new oxide heterostructure interfaces to be investigated, uncovering further structure–property relationships, which are key to optimizing device performance.

**METHODS**

**Film Synthesis, Lift-off, and Enrichment.** A schematic for the film growth and lift-off procedure is shown in Figure S1. All thin films were grown by pulsed laser deposition (PLD) with a KrF excimer laser ($\lambda = 248$ nm) on STO (001) substrates (1 cm $\times$ 0.5 cm), to a thickness of around 1 $\mu$m as measured by a Veeco Dektak 6M stylus profilometer. Poly-crystalline PLD targets were prepared via solid-state synthesis: the as-received precursors were hand-ground before sintering in air at 1350 $^\circ$C, and pelletizing step. Sr$_3$Al$_2$O$_6$ targets were prepared from mixtures of CeO$_2$ (Alfa Aesar, 99.99%) and Al$_2$O$_3$ (Alfa Aesar, 99.97%) powders. CeO$_2$/STO and Gd$_{0.03}$Ce$_{0.97}$O$_{1.95}$/STO targets were prepared from mixtures of CeO$_2$ (Alfa Aesar, 99.9%), SrTiO$_3$ (Sigma-Aldrich, 99.9%), and Gd$_2$O$_3$ (Sigma-Aldrich, 99.9%) as required; the targets comprised a 1:1 molar ratio of the total metal content in the (doped) CeO$_2$ to the STO.

Before deposition of the target films, a Sr$_3$Al$_2$O$_6$ buffer layer was grown on the SrTiO$_3$ (001) substrate at a substrate temperature $T_s = 700$ $^\circ$C with $p_{O_2} = 1 \times 10^{-6}$ mbar, while using a 1.25 J cm$^{-2}$ laser fluence and a repetition rate of 1 Hz for 10 min. The target nanopowder films were then grown in situ at $T_s = 750$ $^\circ$C and $p_{O_2} = 0.2$ mbar, using a 1.5 J cm$^{-2}$ laser fluence and a repetition rate of 5 Hz for 2 h. After deposition, all films were postannealed at 650 $^\circ$C for 1 h under $p_{O_2} = 0.8$ bar to ensure equilibrium oxide stoichiometry.

Poly(methyl methacrylate) (PMMA, Alfa Aesar, $M_w = 950$ kg mol$^{-1}$) was dissolved in anisole (4 wt %, Sigma-Aldrich, 99.7%) and spin-coated (2000 RPM, 30 s) onto the thin film with the substrate, then naturally dried for 12 h to obtain a PMMA layer with a thickness of around 1 $\mu$m. The top half of the rotor. Unenrichment was performed in the same way, but with the quartz tube left open to air during overnight heating.

**Solid-State NMR.** The NMR spectra were recorded on a 9.4 T Bruker Avance spectrometer using a Bruker 1.3 mm HX probe, 50 kHz MAS frequency, and a Hahn echo pulse sequence ($\pi/2 - \tau - \pi - \tau - \text{acquire}$), with recycle delays of 0.1–1 s as specified in the figure captions. Variable-temperature NMR experiments were performed by application of heated nitrogen gas and the sample temperature was determined from an ex situ calibration using the temperature-dependent $^{207}$Pb shift of Pb(NO$_3$)$_2$. The $^{17}$O NMR spectra were referenced to H$_2$O at 0 ppm and deconvoluted using the dmfit program. $T_1$ and $T_2$ relaxation constants, and the errors in these values, were determined by total least-squares refinement of saturation recovery and variable-length Hahn echo data using IGOR Pro.

**DFT Calculations.** Density functional theory (DFT) calculations were performed using the plane-wave pseudopotential code CASTEP$^{25}$ and the general gradient approximation-based PBEsol exchange correlation functional.$^{26}$ The valence states of 2s$^2$ for O, 3s 3p 3d 4s for Ti, 4s 4p 5s for Sr, and 4f 5s 5p 6s 6d for Ce were treated using on-the-fly generated (OTFG) core-corrected ultrasoft pseudopotentials. Due to the large system size, a softer set of pseudopotentials from the QC5 library were used that require lower cut-off energies than the standard CASTEP pseudopotentials from the C18 library. The convergence was checked for the QC5 potential and a plane-wave cut-off energy of 350 eV was found to be sufficient (Figure S10). For one of the interface models, the shielings were calculated with the softer pseudopotentials were then compared to shielings calculated using the default pseudopotentials with a converged cut-off energy of 700 eV (Figure S11); the two pseudopotentials were found to give almost identical results for the STO region and an error of up to 15 ppm for the CeO$_2$ region (Figure S12), which is significantly less than the experimental linewidth ($\sim$115 ppm). Generation settings for both pseudopotential sets are tabulated in Tables S2 and S3. Reciprocal space was sampled with a 1 $\times$ 1 $\times$ 1 Monkhorst–Pack grid for the 0$\overline{0}$ interface and a 1 $\times$ 1 $\times$ 1 grid for the 45$^\circ$ interface (described below). The GIPAW method$^{25,26}$ integrated with CASTEP was used for calculating the NMR shielding of O atoms. The shielding was determined to within 0.1 ppm by fitting to the experimental values of STO and CeO$_2$ (465 and 877 ppm, respectively), using the regression $\delta = -0.5914 \tau + 298.15$; the resulting shifts for the interface are therefore effectively interpolated between those of the pure materials, affording cancellation of any systematic errors in the shielings. The Atomic Simulation Environment (ASE)$^{27}$ was used to prepare input structures and search seeds. DFT calculations were managed and automated using the AiiDA framework.$^{28}$ Structures were visualized using the VESTA software package.$^{29}$

**Interface Models.** The structures for the 0$\overline{0}$ interface were taken from Zhu et al.,$^{30}$ and the same interface structure searching procedures described therein were used here for the 45$^\circ$ interface. For the 0$\overline{0}$ interface, a slab model was used with an overall thickness of ~14 Å, comprising the STO and CeO$_2$ structures with the interface in the middle, surrounded by vacuum; by calculating a thicker slab, the 14 Å slab was shown to be sufficient to converge the NMR parameters for the interface (Figure S13). The outer layers are, however, affected by the external surface and for this reason the shifts of the bulk materials are not reproduced; for instance, the overestimation of the CeO$_2$ $^{17}$O shift away from the interface is consistent with the higher calculated and experimental $^{17}$O shifts for CeO$_2$ surfaces. For the 45$^\circ$ interface, a periodic model was used with two interfaces, as described in the text. The random structure searching was performed by randomizing atomic positions in the first
layers on either side of the interface, subject to species-wise minimal separation constraints, followed by relaxing the ionic positions with fixed cell parameters along the directions parallel to the interface plane, using interatomic potentials as described in Zhu et al.\textsuperscript{17} The simulation cells for the 45° interface contained two equivalent interfaces that are mirror images of each other. The procedure was repeated until the lowest-energy structures had been repetitively found. A total of 8966 candidate structures were generated and evaluated. The lowest-energy structure was further relaxed by DFT and used to compute the NMR shifts.

ASSOCIATED CONTENT

1 Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.chemmater.0c02698.

Details on the methodology, additional \(^{17}\)O NMR spectra, \(^{15}\)N T\(_{1}\) relaxation analysis; DFT structures and additional results; DFT convergence testing; analysis of the orientations of the interfaces; calculated T\(_{2}\) relaxation under two-site exchange (PDF)

Spreadsheet of calculated \(^{17}\)O parameters for different interfacer structures (XLSX)

AUTHOR INFORMATION

Corresponding Author

Clare P. Grey — Department of Chemistry, University of Cambridge, Cambridge CB2 1EW, United Kingdom; orcid.org/0000-0001-5572-192X; Email: cpg27@cam.ac.uk

Authors

Michael A. Hope — Department of Chemistry, University of Cambridge, Cambridge CB2 1EW, United Kingdom; orcid.org/0000-0002-4742-9336

Bowen Zhang — Department of Materials Science and Metallurgy, University of Cambridge, Cambridge CB3 0FS, United Kingdom

Bonan Zhu — Department of Materials Science and Metallurgy, University of Cambridge, Cambridge CB3 0FS, United Kingdom

David M. Halat — Department of Chemistry, University of Cambridge, Cambridge CB2 1EW, United Kingdom; orcid.org/0000-0002-0919-1689

Judith L. MacManus-Driscoll — Department of Materials Science and Metallurgy, University of Cambridge, Cambridge CB3 0FS, United Kingdom

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.chemmater.0c02698

Notes

The authors declare no competing financial interest. The raw data for the NMR and DFT calculations can be found at DOI: 10.24435/materialscloud:4v-04.

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REFERENCES

(1) Ohtomo, A.; Hwang, H. Y. A High-Mobility Electron Gas at the LaAlO\(_3/\)SrTiO\(_3\) Heterointerface. Nature 2004, 427, 423–426.

(2) Hwang, H. Y.; Iwasa, Y.; Kawasaki, M.; Keimer, B.; Nagaosa, N.; Tokura, Y. Emergent Phenomena at Oxide Interfaces. Nat. Mater. 2012, 11, 103–113.

(3) Tokura, Y.; Hwang, H. Y. Complex Oxides on Fire. Nat. Mater. 2008, 7, 694–695.

(4) MacManus-Driscoll, J. L. Self-Assembled Heteroepitaxial Oxide Nanocomposite Thin Film Structures: Designing Interface-Induced Functionality in Electronic Materials. Adv. Funct. Mater. 2010, 20, 2035–2045.

(5) Choi, E.-M.; Di Bernardo, A.; Zhu, B.; Lu, P.; Alpern, H.; Zhang, K. H. L.; Shapira, T.; Feighan, J.; Sun, X.; Robinson, J.; et al. 3D Strain-Induced Superconductivity in La,CuO\(_{4+x}\). Using a Simple Vertically Aligned Nanocomposite Approach. Sci. Adv. 2019, 5, No. eaav5532.

(6) MacManus-Driscoll, J. L.; Foltyn, S. R.; Jia, Q.; Wang, H.; Serquis, A.; Civale, L.; Maiorov, B.; Hawley, M. E.; Maley, M. P.; Peterson, D. E. Strongly Enhanced Current Densities in Superconducting Coated Conductors of YBa\(_2\)Cu\(_3\)O\(_{7-x}\) + BaZrO\(_3\). Nat. Mater. 2004, 3, 439–443.

(7) Gutiérrez, J.; Llordés, A.; Gámez, J.; Gibert, M.; Romà, N.; Ricart, S.; Pomar, A.; Sandiumenge, F.; Mestre, N.; Puig, T.; et al. Strong Isotropic Flux Pinning in Solution-Derived YBa\(_2\)Cu\(_3\)O\(_{7-x}\) Nanocomposite Superconductors. Nat. Mater. 2007, 6, 367–373.

(8) Llordés, A.; Palau, A.; Gámez, J.; Coll, M.; Vlad, R.; Pomar, A.; Arbiol, J.; Guzmán, R.; Ye, S.; Rouco, V.; et al. Nanoscale Strain-Induced Pair Suppression as a Vortex-Pinning Mechanism in High-Temperature Superconductors. Nat. Mater. 2012, 11, 329–336.

(9) Choi, E.-M.; Weal, E.; Bi, Z.; Wang, H.; Kursunovic, A.; Fix, T.; Blamire, M. G.; MacManus-Driscoll, J. L. Strong Room Temperature Exchange Bias in Self-Assembled BiFeO\(_3/-\)Fe\(_3\)O\(_4\) Nanocomposite Heteroepitaxial Films. Appl. Phys. Lett. 2013, 102, No. 012905.

(10) Fix, T.; Choi, E.-M.; Robinson, J. W. A.; Lee, S. B.; Chen, A.; Prasad, B.; Wang, H.; Blamire, M. G.; MacManus-Driscoll, J. L. Electric-Field Control of Ferromagnetism in a Nanocomposite via a ZnO Phase. Nano Lett. 2013, 13, 5886–5890.

(11) Khatkhatay, F.; Chen, A.; Lee, J. H.; Zhang, W.; Abdel-Raziq, H.; Wang, H. Ferroelectric Properties of Vertically Aligned Nanostructured BaTiO\(_3/-\)CeO\(_2\) Thin Films and Their Integration on Silicon. ACS Appl. Mater. Interfaces 2013, 5, 12541–12547.

(12) Harrington, S. A.; Zhai, J.; Denev, S.; Gopalan, V.; Wang, H.; Bi, Z.; Redfern, S. A. T.; Baek, S.-H.; Bark, C. W.; Eom, C.-B.; et al. Thick Lead-Free Ferroelectric Films with High Curie Temperatures through Nanocomposite-Induced Strain. Nat. Nanotechnol. 2011, 6, 491–495.

(13) Zheng, H.; et al. Multiferroic BaTiO\(_3/-\)CoFe\(_2\)O\(_4\) Nanostuctures. Science 2004, 303, 661–663.

(14) Chen, A.; Bi, Z.; Tsai, C.-F.; Lee, J.; Su, Q.; Zhang, X.; Jia, Q.; MacManus-Driscoll, J. L.; Wang, H. Tunable Low-Field Magneto-resistance in (La\(_{0.8}\)Sr\(_{0.2}\)MnO\(_3\))\(_{0.5}\)(ZnO\(_{0.2}\))\(_{0.5}\) Self-Assembled Vertically Aligned Nanocomposite Thin Films. Adv. Funct. Mater. 2011, 21, 2423–2429.

(15) Zhang, W.; Chen, A.; Khatkhatay, F.; Tsai, C.-F.; Su, Q.; Jiao, L.; Zhang, X.; Wang, H. Integration of Self-Assembled Vertically Aligned Nanocomposite [(La\(_{0.8}\)Sr\(_{0.2}\)MnO\(_3\))\(_{0.5}\)(ZnO\(_{0.2}\))] Thin Films on Silicon Substrates. ACS Appl. Mater. Interfaces 2013, 5, 3995–3999.

(16) Cho, S.; Yun, C.; Tappertzhofen, S.; Kursunovic, A.; Lee, S.; Lu, P.; Jia, Q.; Fan, M.; Jian, J.; Wang, H.; et al. Self-Assembled Oxide
Films with Tailored Nanoscale Ionic and Electronic Channels for Controlled Resistive Switching. *Nat. Commun.* 2016, 7, No. 12373.

(17) Lee, S.; Zhang, W.; Khathakhatay, F.; Wang, H.; Jia, Q.; MacManus-Driscoll, J. L. Ionic Conductivity Increased by Two Orders of Magnitude in Micrometer-Thick Vertical Yttria-Stabilized ZrO2 Nanocomposite Films. *Nano Lett.* 2015, 15, 7362–7369.

(18) Yang, S. M.; Lee, S.; Jian, J.; Zhang, W.; Lu, P.; Jia, Q.; Wang, H.; Won Noh, T.; Kalinin, S. V.; MacManus-Driscoll, J. L. Strongly Enhanced Oxygen Ion Transport through Samarium-Doped CeO2 Nanopillars in Nanocomposite Films. *Nat. Commun.* 2015, 6, No. 8588.

(19) Chen, A.; Su, Q.; Han, H.; Enriquez, E.; Jia, Q. Metal Oxide Nanocomposites: A Perspective from Strain, Defect, and Interface. *Adv. Mater.* 2019, 31, No. 1803241.

(20) Yadav, A. K.; Nelson, C. T.; Hsu, S. L.; Hong, Z.; Clarkson, J. D.; Schlepütz, C. M.; Damodaran, A. R.; Shafer, P.; Arenholz, E.; Dedon, L. R.; et al. Observation of Polar Vortices in Oxide Superlattices. *Nature* 2016, 530, 198–201.

(21) Yun, H.; Ganguly, K.; Postiglione, W.; Jalan, B.; Leighton, C.; Mkhoyan, K. A.; Jeong, J. S. Microstructure Characterization of BaSnO3 Thin Films on LaAlO3 and PrScO3 Substrates from Transmission Electron Microscopy. *Sci. Rep.* 2018, 8, No. 10245.

(22) Prencipe, I.; Dellasega, D.; Zani, A.; Rizzo, D.; Passoni, M. Energy Dispersive X-Ray Spectroscopy for Nanostuctured Thin Film Density Evaluation. Sci. *Technol. Adv. Mater.* 2015, 16, No. 025007.

(23) Islam, M. R.; Zubair, M. A.; Bashar, M. S.; Rashid, A. K. M. B. Bi3Ho6Fe6O20/TIO2 Composite Thin Films: Synthesis and Study of Optical, Electrical and Magnetic Properties. *Sci. Rep.* 2019, 9, No. 5205.

(24) Lee, S.; Zhang, W.; Khathakhatay, F.; Jia, Q.; Wang, H.; MacManus-Driscoll, J. L. Strain Tuning and Strong Enhancement of Ionic Conductivity in SrZrO2–RE2O3 (RE = Sm, Eu, Gd, Dy, and Er) Nanocomposite Films. *Adv. Funct. Mater.* 2015, 25, 4328–4333.

(25) Stambouli, A. B.; Traversa, E. Solid Oxide Fuel Cells (SOFCs): An Introduction to the Background Principles and Applications to Inorganic Materials. *Chem. Soc. Rev.* 2006, 35, 718–735.

(26) Wolczky, M.; Repinski, L. Rietveld Refinement of the Structure of CeOCl Formed in Pd/Co3O4/Catalyst: Notes on the Existence of a Stabilized Tetragonal Phase of La2O3 in La-Pd-O System. *J. Solid State Chem.* 1992, 99, 409–413.

(27) Nemles, R. J.; Meyer, G. M.; Hutton, J. High-Resolution (Direct Space) Studies of Anharmonic Motion Associated with the Structural Phase Transition in SrTiO3. *Ferroelectrics* 1978, 21, 461–462.

(28) Zhu, B.; Schusteritsch, G.; Lu, P.; MacManus-Driscoll, J. L.; Pickard, C. J. Determining Interface Structures in Vertically Aligned Nanocomposite Films. *APL Mater.* 2019, 7, No. 061105.

(29) Chadwick, A. V.; Poplett, I. J. F.; Maitland, D. T. S.; Smith, M. E. Oxygen Speciation in Nanophase MgO from Solid-State 17O NMR Spectroscopy. *Chem. Commun.* 2011, 23, No. 053201.

(30) Oldfield, E.; Coretsopoulos, C.; Yang, S.; Reven, L.; Lee, H. C.; Shore, J.; Han, O. H.; Ramili, E.; Hinks, D. 17O Nuclear-Magnetic-Resonance Spectroscopic Study of High-T, Superconductors. *Phys. Rev. B* 1989, 40, 6832–6849.

(31) Bastow, T. J.; Dirken, P. J.; Smith, M. E.; Whitfield, H. J. Factors Controlling the 17O NMR Chemical Shift in Ionic Mixed Metal Oxides. *J. Phys. Chem. A* 1996, 100, 18539–18545.

(32) Hoffstetter, A.; Balodis, M.; Widdifield, C. M.; Stevanato, G.; Pinon, A. C.; Bygrave, P. J.; Day, G. M.; Emsley, L. 17O Nuclear-Magnetic-Resonance Spectroscopic Study of High-Tc Oxide Systems. *Chem. Mater.* 2004, 16, 2142–2146.

(33) Hope, M. A.; Halat, D. M.; Lee, J.; Grey, C. P. A.17O Paramagnetic NMR Study of Sm2O3, Eu2O3, and Sm/Eu-Substituted CeO2, *Solid State Nucl. Magn. Reson.* 2019, 102, 21–30.

(34) McCarry, R. J.; Stebbins, J. F. Transition Metal Doped Cation Distributions in MgO and CaO: New Inferences from Paramagnetically Shifted Resonances in 17O, 54Mg, and 40Ca NMR Spectra. *J. Phys. Chem. C* 2016, 120, 11111–11120.

(35) Fuda, K.; Kishio, K.; Yamauchi, S.; Fueki, K. Study on Vacancy Motion in Y2O3-Doped CeO2 by 17O NMR Technique. *J. Phys. Chem. Solids* 1985, 46, 1141–1146.

(36) Panchmatia, P. M.; Orera, A.; Rees, G. J.; Smith, M. E.; Hanna, J. V.; Slater, P. R.; Islam, M. S. Oxygen Defects and Novel Transport Mechanisms in Apatite Ionic Conductors: Combined 17O NMR and Modeling Studies. *Angew. Chem., Int. Ed. 2011, 50, 9328–9333.

(37) Halat, D. M.; Dervişoğlu, R.; Kim, G.; Dunstan, M. T.; Blanc, F.; Middlemiss, D. S.; Grey, C. P. Probing Oxide-Ion Mobility in the Mixed-Ionic–Electronic Conductor La2NiO4+x by Solid-State 17O MAS NMR Spectroscopy. *J. Am. Chem. Soc.* 2016, 138, 11958–11969.

(38) Pickard, C. J.; Needs, R. J. Ab Initio Random Structure Approximation Formalism for Evaluating Decay of NMR Spin Echoes. *Phys. Rev. B* 1996, 54, 4207–4217.
(55) Viefhaus, T.; Bolse, T.; Müller, K. Oxygen Ion Dynamics in Yttria-Stabilized Zirconia as Evaluated by Solid-State $^{17}$O NMR Spectroscopy. *Solid State Ionics* 2006, 177, 3063–3068.

(56) Van Laethem, D.; Deconinck, J.; Hubin, A. Multiscale Modeling of the Ionic Conductivity of Acceptor Doped Ceria. *J. Eur. Ceram. Soc.* 2020, 40, 2404–2416.

(57) Yu, X.; Liu, Y.; Wang, J.; Isheim, D.; Phatak, C.; Haile, S. M. Variability and Origins of Grain Boundary Electric Potential Detected by Electron Holography and Atom-Probe Tomography. *Nat. Mater.* 2020, 19, 887–893.

(58) Kudo, T.; Obayashi, H. Mixed Electrical Conduction in the Fluorite-Type $\text{Ce}_{1-x}\text{Gd}_{x}\text{O}_{2-x/2}$. *J. Electrochem. Soc.* 1976, 123, 415.

(59) Bielecki, A.; Burum, D. P. Temperature Dependence of $^{207}$Pb MAS Spectra of Solid Lead Nitrate. An Accurate, Sensitive Thermometer for Variable-Temperature MAS. *J. Magn. Reson.*, Ser. A 1995, 116, 215–220.

(60) Massiot, D.; Fayon, F.; Capron, M.; King, I.; Le Calvé, S.; Alonso, B.; Durand, J.-O.; Bujoli, B.; Gan, Z.; Hoatson, G. Modelling One- and Two-Dimensional Solid-State NMR Spectra. *Magn. Reson. Chem.* 2002, 40, 70–76.

(61) Clark, S. J.; Segall, M. D.; Pickard, C. J.; Hasnip, P. J.; Probert, M. J.; Refson, K.; Payne, M. C. First Principles Methods Using CASTEP. *Z. Kristallogr.* - *Cryst. Mater.* 2005, 220, 567–570.

(62) Perdew, J. P.; Ruzsinszky, A.; Csonka, G. I.; Vydrov, O. A.; Scuseria, G. E.; Constantin, L. A.; Zhou, X.; Burke, K. Restoring the Density-Gradient Expansion for Exchange in Solids and Surfaces. *Phys. Rev. Lett.* 2008, 100, No. 136406.

(63) Yates, J. R.; Pickard, C. J.; Mauri, F. Calculation of NMR Chemical Shifts for Extended Systems Using Ultrasoft Pseudopotentials. *Phys. Rev. B* 2007, 76, No. 024401.

(64) Pickard, C. J.; Mauri, F. All-Electron Magnetic Response with Pseudopotentials: NMR Chemical Shifts. *Phys. Rev. B* 2001, 63, No. 245101.

(65) Larsen, A. H.; Mortensen, J. J.; Blomqvist, J.; Castelli, I. E.; Christensen, R.; Dulak, M.; Friis, J.; Groves, M. N.; Hammer, B.; Hargus, C.; et al. The Atomic Simulation Environment—a Python Library for Working with Atoms. *J. Phys. Condens. Matter* 2017, 29, No. 273002.

(66) Pizzi, G.; Cepellotti, A.; Sabatini, R.; Marzari, N.; Kozinsky, B. AiiDA: Automated Interactive Infrastructure and Database for Computational Science. *Comput. Mater. Sci.* 2016, 111, 218–230.

(67) Momma, K.; Izumi, F. VESTA 3 for Three-Dimensional Visualization of Crystal, Volumetric and Morphology Data. *J. Appl. Crystallogr.* 2011, 44, 1272–1276.