Direct visualization of anionic electrons in an electrode reveals inhomogeneities

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Electrides are an unusual family of materials that feature loosely bonded electrons that occupy special interstitial sites and serve as anions. They are attracting increasing attention because of their wide range of exotic physical and chemical properties. Despite the critical role of the anionic electrons in inducing these properties, their presence has not been directly observed experimentally. Here, we visualize the columnar anionic electron density within the prototype electride $Y_3Si_3$ with sub-angstrom spatial resolution using differential phase-contrast imaging in a scanning transmission electron microscope. The data further reveal an unexpected charge variation at different anionic sites. Density functional theory simulations show that the presence of trace H impurities is the cause of this inhomogeneity. The visualization and quantification of charge inhomogeneities in crystals will serve as valuable input in future theoretical predictions and experimental analysis of exotic properties in electrides and materials beyond.

INTRODUCTION

Electrides are a unique class of compound materials that comprise a framework of cation and anion sublattices with a net positive effective charge that is compensated by “anionic electrons” that are loosely bonded and localized at interstitial sites, forming an effective anion sublattice (1–6). Starting in the 1980s, electrides were studied as bulk materials, with several seminal papers highlighting their potential for unconventional physical and chemical properties (1–6). In the past decade, electrides became the focus of a rapidly growing number of papers with the discovery of layered electrides (7, 8), in which the anionic electrons form sheets within the van der Waals gaps between atomic layers, exhibiting very high electron mobility, very small work function, and strong magnetic anisotropy. At about the same time, electrides with anionic electrons localized in one-dimensional (1D) channels gained prominence (9, 10). Very recently, several electrides have been predicted to feature topological behavior (11–13). Overall, anionic electrons in electrides have been demonstrated to exhibit catalytic activity (9, 14, 15), high mobility and unconventional magnetism (7, 8), superconductivity (16, 17), nontrivial topological behavior (11–13), and strong correlations (18) and to behave like solvated ions in solutions (19). Electrides have also been demonstrated to be good for storing hydrogen (20, 21). All these features nurture expectations for real applications. However, electrides have so far been characterized only with macroscopic experiments, such as measurements of the work function (1, 2, 5, 7), while the highly localized anionic charge density has only been studied theoretically (4, 6, 11, 22–24).

Aberration-corrected scanning transmission electron microscopy (STEM) routinely achieves sub-angstrom resolution and has been applied to directly characterize the structural, chemical, and bonding properties of materials at the atomic scale (25–27). While conventional STEM techniques are insensitive to local variations in the charge density, phase-contrast imaging, such as inline electron holography, recently demonstrated the capability to visualize a 2D electron gas with a spatial resolution of several nanometers (28, 29). Concurrently, differential phase contrast (DPC) in STEM, which can be obtained by using either segmented detectors (30–32) or 4D-STEM data sets from a pixilated detector (33, 34), has recently been shown to map local electric fields and charge densities at an unprecedented sub-angstrom spatial resolution (30, 31, 33–36). That capability renders STEM-DPC a powerful potential technique for probing the atomic-scale localization of the charge density at anionic sites in electrides.

In this work, we use STEM-DPC to directly probe the charge density in the interstitial columns of $Y_3Si_3$, a prototype electride, using a pixilated detector (or 4D-STEM). $Y_3Si_3$ contains spatially localized electrons within 1D channels of ~4 Å diameter (9). Previous theoretical calculations determined that these electrons are loosely bonded, occupying electronic states near the Fermi energy, leading to catalytic reactivity for $Y_3Si_3$ (9) and exotic quantum properties, such as superconductivity and Mott-insulating behavior in similar structures (17, 18, 37). Here, we use STEM-DPC to analyze the total charge density in $Y_3Si_3$, and, more specifically, electrons that accumulate at the interstitial columns surrounded by hexagonal rings of six Y atoms. The STEM-DPC results are complemented by density functional theory (DFT) calculations of the electric field and charge density, yielding good agreement between the theoretical results and the experimental data averaged over a large number of columns. However, by analyzing a large field of view of the electride, we find an unexpected variance in the observed anionic charge density at different interstitial columns. DFT simulations suggest that the likely origin of the observed inhomogeneities are H impurities, which are...
known to be ubiquitous in materials, but often difficult to detect in small concentrations.

RESULTS
Crystal structure of Y₅Si₃
Y₅Si₃ crystallizes in a hexagonal Mn₅Si₃-type structure with the P6₃/mcm space group. Its structure in the [001] projection (Fig. 1A) shows six yttrium (Y) atomic columns forming hexagonal rings, each of which is composed of two alternating staggered layers of three Y triangles along the [001] projection. We have marked these atoms as YR on the schematic and the other Y sites as Y₁ to help distinguish between the two for the remainder of the article. The centers of the Y rings form an interstitial column with a diameter of ~4 Å.

Y₅Si₃ crystals were prepared by arc-melting high-purity Y and Si sources, following Lu et al. (9). A powder x-ray diffraction pattern (fig. S1) revealed the synthesized Y₅Si₃ as being a single-phase system in the as-cast ingot, with refined lattice parameters [a = 8.4087(1) Å and c = 6.3422(1) Å] that are consistent with those in a previous report (9). The Y₅Si₃ phase was air stable and water durable, as reported by Lu et al. (9). Ground fine powders were dispersed onto TEM grids in a helium-filled glovebox for the STEM experiments. TEM specimens are exposed to air during specimen loading, which is about 3 min.

Electric field and charge density maps in Y₅Si₃
Figure 1B shows a high-angle annular dark-field (HAADF) image for a 3 nm × 3 nm region of Y₅Si₃ oriented along the [001] axis. Owing to the Z-contrast nature of HAADF imaging (where Z is the atomic number), the intensity increases as the total number of atoms and/or their atomic number increase in each column. Thus, the brightest spots in the HAADF are the Y₁ sites, which have double the number of Y atoms per unit cell as the YR sites. The YR atoms of the hexagonal ring are visible (and marked in the schematic in Fig. 1B), while the Si atoms are not observed in the HAADF images because of their proximity to the heavier Y atoms. The invisibility of Si atoms in HAADF images is confirmed by STEM image simulations, as shown in fig. S2.

In the DPC experiment, the electron beam is rastered across the region of interest (ROI) and the convergent-beam electron diffraction (CBED) pattern is measured by a high-speed pixelated detector to form a 4D-STEM dataset. Because only the direct beam is used for 4D-STEM, a HAADF image can be acquired simultaneously without disrupting the DPC acquisition. For each probe position in the 4D-STEM dataset, the gradient of the electrostatic potential, i.e., the electric field in the sample, can be determined by measuring the shifts in the center of mass (CoM) of the CBED pattern. For thin objects, CoM shifts are proportional to the electric field experienced by the incident electron beam, allowing atomic-scale mapping of the local electric fields and charge densities (33, 35, 38).

Figure 2 shows a DPC acquisition of Y₅Si₃ with an interstitial column in the middle. The simultaneously acquired HAADF image is shown in Fig. 2A. A schematic of how different signs of charge influence the CBED pattern and result in CoM shifts is shown in Fig. 2B; near a localized positive charge the incoming electron beam experiences a Coulomb attraction, whereas near a localized negative charge density the electron beam experiences Coulomb repulsion, while both result in a measurable shift of the distribution of electrons within the central disc of the CBED pattern.

The deflection of the beam in milliradians can be converted to a momentum transfer for each probe position, and for thin specimens (less than 5 nm), the momentum transfer can be quantitatively related to the projected electric field via Ehrenfest’s theorem (38–40). Using position-averaged CBED (PACBED) from the dataset, we measured our sample to be ~7 unit cells thick (corresponding to a thickness of 4.4 nm that is supported by electron-energy loss spectroscopy log-ratio analysis) (see figs. S3 and S4 for more details), allowing us to convert the CoM shifts into the projected electric field of the electrode, as shown in Fig. 2C.

At the Y₁ sites, we observe the characteristic DPC profile of an atomic column corresponding to highly localized positive charge: a toroidal intensity profile, centered at the nucleus, with a radially outward directional profile. Although the CoM shifts corresponding to each probe position are the combined result from the electron cloud, the nuclei, and chemical bonding, it is the highly localized positive nuclear charges that dominate the atomic columns. However, the interstitial column is well isolated from its nearest atoms, i.e., YR atoms. The distance between the interstitial column center to its nearest YR columns is ~2.05 Å in the beam projection. The electric field surrounding the interstitial column center—i.e., the centers of the YR hexagonal ring—has the same toroidal intensity profile but...
with a radially inward directional profile, indicating that the region contains spatially localized negative charge.

The projected electric field vectors can be converted to the projected charge density through Gauss’s law, allowing us to examine the localization of charges directly and quantitatively, as plotted in Fig. 2D. As expected, the Y₁ and Y₈ sites are positive, corresponding to the high proton density, and are maximized at the positions of the nuclei, while in the interstitial column we observe a distinct negative charge density, consistent with the theoretically predicted anionic electrons for the electride. We note that such an electric field profile could also be produced simply from probe tails interacting with the nuclei surrounding the site, as was reported previously for graphene (32). However, in this case, the contributions from the surrounding Y ring are mitigated because the implemented experimental probe size is ~1 Å (full width at half maximum), while the distance between the six Y₈ and the center of the interstitial site is much larger, ~2 Å. To confirm the detection of anionic electrons, comparisons of DPC experimental results with the simulated charge density from DFT calculations can provide a trustworthy view of the charge density distribution in materials (34, 38, 39).

Comparisons of DPC measurements with simulated charge density from DFT

To better understand the DPC measurements, DFT calculations were performed to determine the charge density in the interstitial columns in Y₅Si₃. As shown in Fig. S5, calculations confirm the presence of localized electrons in the interstitial columns. These interstitial electrons mainly sit within 1 eV from the Fermi energy (Fig. S6) and are largely contributed by anionic electrons, as reported by Lu et al. (9).

Validation of DPC measurements is performed by comparing the experimental observations of an interstitial unit cell (Fig. 3A) with the total charge density map calculated using DFT calculations (Fig. 3B), which has been proven to be an effective method. Here, the DFT total charge density map (Fig. 3B) is constructed by combining the electron density (obtained directly from the DFT calculation) with the proton density (obtained from positions and charges of the point nuclei in the projected field of view). Both the electron and proton densities were convolved with a probe function to match the spatial resolution of the electron beam, before being combined to form the total charge density (see detailed methods in fig. S7). Pseudopotentials, which treat the nuclei and core electrons together as screened nuclei with finite radii, were used in calculations. All-electron DFT calculations were also performed to validate the use of pseudopotentials. As shown in fig. S8, the electric field profile and electron density at the interstitial region are both nearly identical to the results obtained from the pseudopotential calculations, confirming the reliability of the calculations.

As shown in Fig. 3, the charge density map from DPC measurements matches well with that from DFT calculations: Both exhibit

Fig. 2. Differential phase contrast in Y₅Si₃. (A) HAADF image of an interstitial column in Y₅Si₃. (B) Schematics for beam interaction with positive and negative charge densities generating CoM shifts. (C) Projected magnitude and direction of the electrostatic field in the sample as obtained from the CoM shifts. (D) Charge density derived from the divergence of the CoM shifts. The charge density color scale displays positive values on a white-to-red scale, negative values on a white-to-blue scale, and net zero charges as white. Note that the bonding electrons between Y and Si atoms are not discernible in (D) because of the broadened nuclear charges. The interstitial electrons, which are the focus of this work, are seen in blue in the column at the center of the map.

Fig. 3. Quantitative comparison to theory. The total charge density in an interstitial unit cell of Y₅Si₃ as determined by (A) DPC and (B) DFT showing a strong qualitative match for the entire unit cell charge profile. (C) Line profiles [across the anionic column, from the regions highlighted with dashed lines in (A) and (B)] for both methods. The average charge density is calculated for the center (1-Å radius) region (marked by the gray area) of each interstitial column, demonstrating an excellent quantitative match between theory and experiment.
similar charge density profiles around a single unit cell; both consist of highly localized positive charge densities of the nuclei at each atomic site; both show a constantly negative charge density throughout the interstitial column; and both resolve the same spacing distances between the Y₁ site and Y₂/Si atoms. These agreements are encouraging, as they indicate that the directions of the CoM shifts are consistent with the gradient of the potential. It has been shown that for samples that are too thick to perform quantitative DPC, the direction of the measured field tends to deviate notably (38).

Quantitative comparisons between DFT and DPC results are shown in Fig. 3C, where line profiles of the respective charge densities across the interstitial column are compared. While the DPC profile shows a slight asymmetry, the average experimental charge density at the column center is in excellent agreement with the calculated value, −0.73 e/Å² for DFT and −0.72 e/Å² for DPC, respectively. Methods of finding the center of the interstitial columns and averaging the column charge density are based on atomic positions obtained from corresponding simulated bright-field images and are described in detail in fig. S9. Results in Fig. 3 therefore demonstrate that DPC is sufficiently sensitive to probe local charge densities at the atomic scale, and comparisons of DPC and DFT measurements provide quantitative information of localized anionic electrons in electrides.

It is noted that, in contrast to the interstitial sites, relatively large intensity differences between DFT and DPC measurements are observed on Y sites. This disparity is largely induced by the dynamic scattering effect in electron imaging and the pseudopotentials adopted in the DFT calculations, because the former imposes a more dominant effect on heavy elements compared to light elements (38, 41, 42), while the latter treats the nuclei and core electrons together as screened nuclei with finite radii. While these factors likely do limit the quantitative comparison between the DPC and DFT results at the atomic sites, the region of the electride that we care most about, namely, the anionic electron columns, is spatially isolated from the atomic nuclei and is not influenced by dynamic scattering in this case.

**Inhomogeneity of anionic charge density in Y₅Si₃**

The ability to quantitatively probe the electrons at the atomic scale allows us to examine the distribution of anionic electrons within the specimen. The charge density map of a relatively large region, shown in Fig. 4A, reveals an unexpected phenomenon—the presence of a qualitative and quantitative inhomogeneity in the charge density profile across the different interstitial columns. Four distinct unit cells were highlighted in Fig. 4A for a further quantitative comparison. Horizontal line profiles of the average charge density in each unit cell are plotted against the corresponding profile from the DFT, as shown in Fig. 4 (B to E). The variation of charge density at the anionic electron sites (the intensity of the middle of the line profile) can be clearly seen. Unit cells C1 and C2 (Fig. 4, B and C) show a close quantitative match with the DFT column charge density, similar to that we analyzed in Fig. 3. Instead, unit cells C3 and C4 (Fig. 4, D and E) present a nearly neutral charge density at the center of the anionic column and deviate from the expected negative charge density. Quantitative analysis of spatial averaging of the charge densities within the center region of 1-Å radius allows us to further determine the average charge density of each cell to be 0.76, 0.75, 0.23, and 0.39 e/Å², respectively. Such an intensity variation suggests that most anionic columns have the predicted negative electron density, while some sites deviate from the pristine anionic charge density and show a lowered electron charge density. Further, these results also demonstrate that DPC not only is sensitive enough to probe small charge densities at the atomic scale but also enables direct atomistic analysis of the charge density in electrides through the combination with DFT calculations.

It is recognized that experimental artifacts could potentially be present in the measurements, but they are not likely to be the cause of the inhomogeneous charge density. First, the heterogeneity is randomly distributed across the 36 columns, while experimental artifacts, primarily induced by specimen thickness or beam illumination conditions, would vary in a rather continuous way. For instance, potential errors induced by beam tilts from scanning would induce systematic differences in the electric field between the top-left and bottom-right corners in each experimental map and introduce approximately the same effect to the interstitial columns as to their nearby atoms, neither of which was observed in our experimental data, as shown in Fig. 4A and figs. S10, S12, and S13.

In addition, no corresponding qualitative changes to the Y or Si intensities are associated with the DPC charge density variation in

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**Fig. 4. Inhomogeneity of anionic charge density of Y₅Si₃.** (A) Charge density map of a large area of Y₅Si₃ showing an inconsistent profile across the center of the interstitial columns. (B to E) Zoomed-in views of columns having both the uniform negative electron density of the electrode (B and C) and an inhomogeneity in the anionic electrons observed across the entire dataset (defined by a sharp peak of close to neutral charge density at interstitial column center) (D and E). (F to I) Line profiles across the column centers compared to the DFT line profile from Fig. 3, demonstrating that columns that do not show the inhomogeneity peak match quantitatively with the predicted DFT charge density (F and G), and the ones that have the inhomogeneity show the sharpest difference directly at the column center (H and I).
anionic columns, as shown in Fig. 4 (B to E) and fig. S10, where quantitative charge density of anionic columns and their surrounding YR columns from a larger region of the specimen are shown to confirm that there is no correlation between the column and its surrounding YR charge densities. Such an independence between the variations in interstitial columns and their neighboring YR columns again indicates that electron beam (e.g., scanning noise and beam tilts), specimen thickness, and surface contamination are unlikely to be the cause.

Moreover, the variation in charge density distributions is higher for Y columns compared to that of interstitial columns, which were calculated to be ±35% for one of the YR columns and ±19% for the interstitial columns, respectively (fig. S11), showing that the inhomogeneity observed among the interstitial columns is genuine. Further validation of the presence of charge variation among anionic columns is obtained by examining charge density maps from specimen regions with different thickness and using multiple different experimental conditions (fig. S12). The inhomogeneity is observed randomly distributed across the different columns in every dataset, demonstrating that the effect can be observed repeatably and that it is real.

Furthermore, the inhomogeneity among the interstitial columns is also proved not to originate from scanning noise, as shown in fig. S13, which overlays the field shift directions on top of the charge density maps for a single unit cell that exhibits deviated charge density and for a unit cell that features the expected charge density. The field directions show that the charge density profile is consistent in both the fast-scanning (x direction) and slow-scanning (y direction) directions. These extensive tests and discussions indicate that while the presence of these potential effects cannot be completely excluded from our DPC experiments, neither of them could be the key cause of the observed inhomogeneity. Instead, such a large inhomogeneous distribution should be associated with a real feature in the material itself.

**Origin of charge density inhomogeneity in anionic columns**

The column-resolved inhomogeneity could not have been observed in other experiments on electride materials, because, so far, only macroscopic techniques, which are insensitive to these local variations, have been used to characterize the presence of anionic charges. Potential origins of the inhomogeneity in anionic columns are lattice defects in YR sites or impurity atoms at anionic sites. The contrast variation of YR atoms in STEM-HAADF images (e.g., Fig. 1B and figs. S2 and S3) is very small, while a missing YR atom should be clearly visible in STEM images if present, considering the specimen thickness, which only contains seven atoms in total per YR column. Impurity atoms are potentially present in the interstitial sites. Considering the zero contrast in STEM-HAADF and the small contrast in DPC images, the only possible impurity is hydrogen.

To illustrate the possibility that H atoms in the interstitial columns cause the observed inhomogeneity, we calculate the total charge density via DFT in the presence of different numbers of H atoms per interstitial column. Figure 5 (A to F) shows charge density plots in the cases of 0, 1, 2, 5, 10, and 20 H atoms per 10 unit cells, hence fractional values of 0, 0.1, 0.2, 0.5, 1, and 2 H atoms per interstitial site or half those values for formula unit (additional details shown in fig. S14). It can be seen that the charge density observed in the center of the column is sensitive to H concentrations. More critically, the incorporation of H results in a partial charge cancellation at the very center of the interstitial columns that is similar to the inhomogeneity observed in DPC. These total charge density maps are therefore directly comparable to the experimental maps obtained from DPC imaging. The intensity line profiles across their anionic columns are then plotted in Fig. 5G, and an apparent dependence of the charge density at the anionic site on the concentration of H can be seen. The charge density values averaged at the center of these reference interstitial columns (1-Å radius region) and their polynomial fits are further plotted in Fig. 5H, showing a nearly linear relationship between charge density and the concentration of H/site.

We can then use this relationship as a reference to estimate the H concentration of each single interstitial column in the specimen. The interstitial columns analyzed in Figs. 3 and 4 are plotted on this line to establish estimates for the H incorporation. The unit cells in Fig. 3, as well as those in Fig. 4 (B and C), are apparently pristine (zero H), while those in Fig. 4 (D and E), which showed a near neutral charge density at the column center, are estimated to have about 1.2 H and 1.9 H per interstitial site, respectively. Moreover, the average H integration of all interstitial columns in Fig. 4A can be
found on the plot as ~0.6 H atom/site, on the basis of its average charge density of \(-0.56 \text{ e/Å}^2\) (fig. S11). In view of the ultrahigh synthesis temperature (>2000°C) and a very short time ambient exposure (~3 min) of the specimen, such a high fraction per site indicates that Y\(_5\)Si\(_3\) incorporates H atoms quite easily. This result is consistent with an earlier report that, under high H\(_2\) pressure and at an elevated temperature, the H concentrations in Y\(_5\)Si\(_3\) can be as high as six per formula unit (20). The energy barrier for a H atom to enter the interstitial column from the surface, calculated by manually stepping the H atom out of the crystal using DFT, is ~0.5 eV (fig. S16), which is an upper bound so that more sophisticated calculations are not necessary. Such a barrier is sufficiently low for H to enter the lattice at room temperature, explaining experimental observations. The possibility of carbon contaminants, a common phenomenon during TEM observations, can be excluded because of the high positive contrast that even one single carbon atom can induce (fig. S15). Electronic excitations at room temperature can also be ruled out, because the density of excited electrons is relatively small even if one assumes that electronic excitations are local as opposed to Bloch-like. Therefore, H integration is most likely the cause for the inhomogeneity observed.

Inelastic neutron scattering (INS) spectroscopy (see Materials and Methods) was used to provide direct evidence for the presence of H in samples prepared using the same synthesis conditions and experiencing similar ambient exposure as the STEM sample. The result is shown in Fig. 6. To identify the peak position contributed by H, DFT phonon calculation was performed using Phonopy (43) for pristine Y\(_5\)Si\(_3\) and 0.5H-Y\(_5\)Si\(_3\). The results were used as input to the OCLIMAX software (44) to simulate INS spectra. The experimental spectrum is compared with the simulated spectra in Fig. 6. Here, we see that below ~350 cm\(^{-1}\) the vibrational response is dominated by Y and Si vibrational modes, and an excellent match is observed between the experiment and both the hydrogenated and pristine simulations. However, above 350 cm\(^{-1}\), no significant vibrational modes are observed in the pristine simulation, but in the hydrogenated simulation and the experiment, we see significant vibrational intensity in this regime, confirming the presence of a significant concentration of H in the material. The possibility of these two distinctive peaks originating from surface absorption of OH can be ruled out, as the typical frequency range for the vibration band of surface OH is 400 to 1000 cm\(^{-1}\), with strong intensities at lower frequencies, and then decays with increasing frequency, a peak profile quite different from the experimental spectrum (45). The presence of two peaks observed in a similar frequency range in the experimental spectra proves the existence of H in the sample.

Using the simulations in Fig. 6, we estimated the H concentration in the sample, as measured by INS to be of order 0.2 H per site, which is within the error bars of the value of the DPC quantification shown in Fig. 5H, 0.6 ± 0.5 H per site (there exists one site per two formula units). We note that the STEM experiments are performed on the absolute thinnest sample area (thickness, ~5 nm), while the powder used for INS has predominantly micrometer-scale dimensions (fig. S17). Thus, the surface-to-volume ratio could play a significant role in the difference between the INS and DPC values. However, both techniques strongly indicate that a high concentration of hydrogen is present in the material and support the conclusion that H is the origin of the observed inhomogeneity in the measured anionic charge density.

**DISCUSSION**

Our knowledge on anionic electrons in electrides, including their origin, distribution, and function, is still in its infancy. This work provides a technique that directly visualizes and quantifies anionic electrons, providing an unprecedented tool to the research of electrides. Detection and quantification of charge variation at anionic electron sites that is revealed and confirmed in this work can be used as input to the analysis of the exotic properties in electrides, in both experimental and theoretical studies, to help understand electrides better. The ability to directly probe spatially distributed electrons in materials opens up new opportunities to exploit real-space charge distributions, e.g., anionic electrons in electrides, the local charge redistribution caused by Moiré superlattices in bilayer 2D materials (46, 47), or the 2D electron gas that forms at some oxide interfaces (48, 49), to tailor these exciting materials for energy and quantum applications.

**MATERIALS AND METHODS**

**Bulk sample preparation**

Polycrystalline Y\(_5\)Si\(_3\) sample was prepared by directly arc-melting high-purity yttrium (99.99% pure; AMES) and Si (99.9999% pure; Alfa Aesar) elements with a molar ratio of 5:3 (9). Before melting, the arc-melter chamber was evacuated and back-filled with Ar for a few times. Zr was used as an oxygen getter and melted before Y and Si were arc-melted. The melted button was flipped over and remelted for five times to create a homogeneous sample. The weight loss during arc-melting was less than 0.1 mass %. The obtained ingot is extremely stable under air and also water durable (9). Nevertheless, after arc-melting, the ingot was transferred immediately into a He-filled glovebox for grinding and TEM specimen preparation.

**X-ray diffraction**

Room temperature powder x-ray diffraction pattern was recorded on a PANalytical X’pert Pro MPD powder diffractometer using Cu K\(_{\alpha1}\) radiation. Powder data were analyzed using the WinCSD program package (50).

**STEM data acquisition**

All the STEM data were acquired on a dedicated aberration-corrected Nion UltraSTEM100 equipped with a cold field-emission electron
source, operated at an accelerating voltage of 100 kV. The probe is ~20 pA with a convergence semi-angle of 30 mrad. HAADF-STEM images were collected using the ~86 to 200 mrad semi-angle range.

DPC imaging was performed on a Nion 2020 Ronchigram camera, with a Hamamatsu ORCA ultra-low noise scientific CMOS sensor and a 2048 × 2048 pixel display. This camera can operate at a rate of 400 megapixels/second, with a readout noise of 1.6 well e− (root mean square). The display readout capability for this camera is between 400 megapixels/second, with a Hamamatsu ORCA ultra-low noise scientific CMOS sensor.

DFT calculations
DFT calculations based on pseudopotentials were performed using the VASP package (51). All-electron DFT calculations were performed using ELK (52). We used the projector augmented wave (53) pseudopotential method and the Perdew-Burke-Ernzerhof (PBE) (54) generalized gradient approximation (GGA) for exchange and correlation. The GGA-PBE pseudopotentials are found to produce more accurate lattice constants than the local density approximation as shown in Table S1. The unit cell was relaxed with a convergence of 10−8 eV for the total energy cutoff is 500 eV. The electronic k-space integration was performed with the tetrahedron method, involving a Γ-centered 12 × 12 × 16 k-mesh. In the DFT calculations, the unit cell is divided into a 128 × 128 × 6 mesh for the charge density, electrostatic potential, and electric field. We also performed calculations using a 2 × 2 × 1 supercell. The resulting charge density, electric field, etc. are the same as using unit cell.

HAADF and PACBED simulations
The HAADF image and PACBED simulations were performed using the frozen phonon model with a 100-kV probe with a probe-forming aperture semi-angle of 30 mrad via μSTEM code (55). A supercell of 67.2 Å × 72.7 Å viewed along the [110] orientation comprising 256 × 256 pixels was used. By comparing experimental PACBED with the simulations, we determined that the experimental specimen thickness is 7 unit cells (= 44.1 Å) (Fig. S3). The experimental defocus was set in the middle of the specimen thickness, and therefore, we used C1 = 22 Å in the simulation.

INS spectroscopy
The INS spectrum of the sample was measured at the VISION beam line at the Spallation Neutron Source (Oak Ridge National Laboratory), an accelerator-based pulsed neutron source operating at 1.4-MW proton beam power. VISION is an inverted geometry spectrometer for neutron energy loss vibrational spectroscopy. It measures incident neutron energy by time of flight. The final neutron energy (3.5 meV) is set by a series of curved pyrolytic graphite mirrors. The dynamic range is from 0 to 8000 cm−1 with a nearly uniform resolution of 1 to 1.5% across this dynamic range. The sample was then cooled to 5 K in a top-loading, closed-cycle refrigerator at the beam line and measured for ~10 hours. The spectrum of the empty sample holder was subtracted to obtain the signal from the sample. INS quantification is performed by using 0.5H-Y2Si3 as a reference and calculating the relative intensity of scattering by H versus that by the bulk crystal (energy transfer region, 20 to 300 cm−1).

SUPPLEMENTARY MATERIALS
Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/7/15/eabe6819/DC1

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