Identifying quasi-2D and 1D electrides in yttrium and scandium chlorides via geometrical identification

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Developing and understanding electron-rich electride offers a promising opportunity for a variety of electronic and catalytic applications. Using a geometrical identification strategy, here we identify a new class of electride material, yttrium/scandium chlorides Y(Sc)Cl$_3$ (y < 2). Anionic electrons are found in the metal octahedral framework topology. The diverse electronic dimensionality of these electrides is quantified explicitly by quasi-two-dimensional (2D) electrides for [YCl]$^-$-$\text{e}^-$ and [ScCl]$^-$-$\text{e}^-$ and one-dimensional (1D) electrides for [Y$_2$Cl$_3$$^-$-$\text{e}^-$, [Sc$_2$Cl$_{10}$]$^+$-$\text{e}^-$, and [Sc$_2$Cl$_{12}$]$^+$-$2\text{e}^-$ with divalent metal elements (Sc$^{2+}$: 3d$^1$ and Y$^{2+}$: 4d$^1$). The localized anionic electrons were confined within the inner-layer spaces, rather than inter-layer spaces that are observed in A$_2$B-type 2D electrides, e.g., Ca$_2$N. Moreover, when hydrogen atoms are introduced into the host structures to form YCl and Y$_2$Cl$_3$H, the generated phases transform to conventional ionic compounds but exhibited a surprising reduction of work function, arising from the increased Fermi level energy, contrary to the conventional electrides reported so far. Y$_2$Cl$_3$ was experimentally confirmed to be a semiconducor with a band gap of 1.14 eV. These results may help to promote the rational design and discovery of new electride materials for further technological applications.

ARTICLE

INTRODUCTION

The design and synthesis of new materials with desirable properties is essential for advancing material applications and innovations, which may influence the future of technology. One example is the recent development of electride materials that significantly promote the catalytic transformation of molecular dinitrogen into ammonia at mild reaction conditions. Electrides is a unique class of materials where the electrons are spatially confined in the vacant crystallographic sites and serve as anions to maintain charge neutrality. The intrinsic characteristics of electrides should suggest superior electronic performances. However, the first proposed organic electrides were thermally unstable and air sensitive, constraining their technological applications. In 2003, a room-temperature stable inorganic electride of Ca$_2$Al$_2$O$_{4d}$ (4e$^-$) was successfully synthesized by Matsuishi et al. and exhibited versatile applications in many areas, including catalysts, anode materials, and an electron-injection layer in organic light-emitting diodes (OLEDs). Subsequently, Ca$_2$N was identified experimentally to be a layer-like two-dimensional electride and can be exfoliated into nanosheets. The Y$_2$C electride was also realized experimentally and furthered our understanding of the interplay between magnetism and localized electrons. These findings of inorganic electrides provide new possibilities for both fundamental science and applications.

Considerable experimental and theoretical investigations have been carried out to discover and produce new electrides with superior functions and capabilities. Usually, researchers arbitrarily alter the elemental combinations of typical electrides but retain their crystal symmetry to extend for the new electrides, e.g., AB-type, A$_2$B-type, and A$_2$B$_2$-type (A = alkaline or rare earth elements, B = IV, V, VI, and VII elements) electrides. Besides, many electrides (e.g., Li$_2$, Na$_2$, Mg$_2$, C$_2$, Na$_2$He$_2$, and Sr$_2$P$_2$) have been found to reveal a generalized structure under pressure. Depending on the dimensionality of the anionic electrons localizations, electrides can be classified into 0D, 1D, and 2D systems, where the anionic electrons are either isolated or bonded with each other in the cage-like, channel-like, or layer-like voids. These interesting results suggest a geometrical way to obtain the diverse 'interstitial spaces' in a lattice that can stabilize excess electrons, which can provide a vast configuration space for computational discovery.

To explore new electrides, we propose a simple strategy for identifying them by checking the local connectivity of pre-existing compositions and structures with high open frameworks. Applying high-throughput ab initio screening strategy based on the Materials Project platforms and Inorganic Crystal Structure Database (ICSD), we focused on the reduced rare-earth yttrium and scandium chlorides (R$_2$Cl$_x$ R = Y, Sc and y: x < 2, i.e., YCl$_{10}$, Y$_2$Cl$_9$, ScCl$_{10}$, Sc$_2$Cl$_{10}$, Sc$_2$Cl$_{12}$, and Sc$_2$Cl$_{13}$). The reduced rare-earth halides were first reported in Gd$_2$Cl$_3$. Later, a series of...
The metal octahedra are stretched in these structures and the \( R \) sharing for variable \( R \)–Cl layers in the layer-like crystal structures. The octahedral volumes of \( Y \) octahedrons varied from 3.30 to 3.85 Å and the shorter \( Y-Y \) separation (3.30 Å in shared edges) suggests a stronger \( Y-Y \) interaction connected to its phase stability.\(^{40,54}\) Despite being congeners of the yttrium element, the \( Sc-Cl \) system has stable stoichiometries of \( ScCl, Sc_5Cl_8, \) and \( Sc_7Cl_{10} \).\(^{40,42,43}\) ScCl crystallizes in the same structure as YCl, containing layer-like interstitial spaces formed by edge-sharing \( Sc \) octahedrons. Channel-like voids in \( Sc_2Cl_6 \) (Fig. 1c) and \( Sc_2Cl_{10} \) (Fig. 1d) are analogous to that of \( Y_2Cl_2 \). Due to the distortion of the \( Sc \) octahedrons, the \( Sc-Sc \) bond distances change within the range of 3.26–0.52 Å for \( ScCl \), 3.10–3.57 Å for \( Sc_5Cl_8 \), and 3.13–3.55 Å for \( Sc_7Cl_{10} \), respectively. The shared edge in the \( Sc \) octahedral chains has the minimum \( Sc-Sc \) distance, comparable to that of metal \( Sc (3.26 \text{ Å}). \)

To evaluate the formation possibilities of interstitial electrons in \( Y-Cl \) and \( Sc-Cl \) compounds, we compared the configuration of interstitial voids in \( Y-Cl \) and \( Sc-Cl \) with other rare-earth-metal-containing electrides, e.g. \( A_2B \)-type compounds (anti-CdCl\(_2\) structure: \( Y_2C, Gd_2C, Tb_2C, Dy_2C, Ho_2C, Er_2C, Sc_2C, Y_2N, La_2N, \) and \( La_2Bi; Cu_2Sb \)-type structure: \( Sc_2As, Sc_2Sb, Sc_2Bi, Y_2Sb, \) and \( Y_2Bi; others: Sc_2N, Y_2As, Y_2O, Y_2S, La_2C, La_2As, La_2Sb, La_2O, \) and \( La_2S, La_2H_2, \) and \( YH_2; \) \( A_5B \) with \( Mn_5Sb \)-type structure \( (Y_2BiSb, Y_2SiSb)_{13,59} \) and \( LaScSi \).\(^{13}\) Metal octahedron severing as interstitial voids can be observed in most of the host structures except \( Y_2O \) and \( A_2B \) with \( Cu_2Sb \)-type structure \( (Sc_2As, Sc_2Sb, Sc_2Bi, Y_2Sb, \) and \( Y_2Bi). For \( Cu_2Sb \)-type \( A_2B \) compounds, the interstitial voids can be viewed to be pseudo-octahedron \( (R_3X) \), in which the octahedron is built by five cations and one anion. To compare the interstitial volume with previously proposed electrides, the octahedral volumes of \( Y-X \) and \( Sc-X \) compounds were plotted in Fig. 2a, b. We can see that the interstitial volumes in \( Y-Cl \) (Fig. 2a) and \( Sc-Cl \) (Fig. 2b) are much higher than those of \( Cu_2Sb \)-type structure (e.g. \( Y_2Sb \) and \( Sc_2As \)), but comparable to the anti-CdCl\(_2\)-type \( Y_2N \) and \( Sc_2N \). The interstitial voids in these compounds proposed here are thus believed to have large enough space to trap anionic electrons.

**RESULTS AND DISCUSSION**

**Structural properties**

The crystal structures of the reduced yttrium and scandium chlorides \((R_2Cl_3, R=\text{Y, Sc}, x<2)\) are characterized by the edge-sharing \( R \) octahedral layer-like (YCl and ScCl), channel-like \((Y_2Cl_3\) and \( Sc_2Cl_6 \)), and double channel-like \((Sc_5Cl_8\) and \( Sc_7Cl_{10} \)) atomic voids in the host structures (Fig. 1). These voids are coated by Cl atoms and formed by variable \( R-Cl \) layers in the layer-like crystal structures. The metal octahedra are stretched in these structures and the \( R-R \) distances on the shared-edges are much shorter than the others. YCl crystallizes into a ZrCl\(_2\)-type structure (\( R-3m \)).\(^{50,51}\) The \( Y_6 \) octahedral layers (Fig. 1a) were distorted and sheathed with chlorine atoms to form \( Cl-Y-Y-Cl \) close-packed layers with an interlayer distance of 3.56 Å. Two distinct \( Y-Y \) separations of 3.57 Å (shared edge) and 3.73 Å can be found in the \( Y_6 \) octahedrons that are comparable with those of 3.56 and 3.80 Å in \( Y_5Si_3 \) electride.\(^{52}\) \( Y_2Cl_3 \) (Fig. 1b) is isostructural to \( Gd_2C_3 \) and \( Tb_2C_3 \) \((Cl=\text{Cl and Br})\).\(^{44,53}\) The \( Y-Y \) distances in the \( Y_6 \) octahedra varied from 3.30 to 3.85 Å and the shorter \( Y-Y \) separation (3.30 Å in shared edges) suggests a stronger \( Y-Y \) interaction connected to its phase stability.\(^{40,54}\) Despite being congeners of the yttrium element, the \( Sc-Cl \) system has stable stoichiometries of \( ScCl, Sc_5Cl_8, \) and \( Sc_7Cl_{10} \).\(^{40,42,43}\) ScCl crystallizes in the same structure as YCl, containing layer-like interstitial spaces formed by edge-sharing \( Sc \) octahedrons. Channel-like voids in \( Sc_2Cl_6 \) (Fig. 1c) and \( Sc_2Cl_{10} \) (Fig. 1d) are analogous to that of \( Y_2Cl_2 \). Due to the distortion of the \( Sc \) octahedrons, the \( Sc-Sc \) bond distances change within the range of 3.26–0.52 Å for \( ScCl \), 3.10–3.57 Å for \( Sc_5Cl_8 \), and 3.13–3.55 Å for \( Sc_7Cl_{10} \), respectively. The shared edge in the \( Sc \) octahedral chains has the minimum \( Sc-Sc \) distance, comparable to that of metal \( Sc (3.26 \text{ Å}). \)

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Electron localization function (ELF) analysis

To uncover the underlying electron characteristics of R$_6$Cl$_6$, we first carried out analysis of the ELF of each phase. Interestingly, as shown in Fig. 3a (YCl), Fig. 3b (Y$_2$Cl$_3$), and Fig. 3c (Sc$_7$Cl$_{10}$), two distinct ELF attractors (non-nuclear maxima in the ELF maps) off the nuclei can be observed in the center of the R$_6$ tetrahedra (green circle in the ELF maps, site A) and R$_8$ octahedra (red circle in the ELF maps, site B). The ELF attractors are more localized in the R$_6$ tetrahedra but dispersed in the R$_8$ octahedra. Further, the finite value of ELF between these two distinct ELF attractors suggests there is a strong interaction between them, due to their short separation (2.31 Å in YCl, 2.44 Å in Y$_2$Cl$_3$, and 2.11 Å in Sc$_7$Cl$_{10}$). However, the interspace in the R$_8$ octahedra is not large enough to hold interstitial electrons, so these ELF attractors may originate from the hybridization of the R-$d$ orbitals, ruling out the possibility of anionic electrons in this configuration. The origin of the ELF attractors in R$_6$ tetrahedra is discussed in the following section. The ELF attractors observed in the metal octahedra are expected to be originated from interstitial electrons; further examinations were performed by analyzing the band structure and partial charge density.

Band structure and magnetic property

Considering the similarity in the metal frameworks of the Sc–Cl and Y–Cl systems, the band structure, and partial charge density of specified bands for YCl and Y$_2$Cl$_3$ and total and projected densities of states (TDOS and PDOS) of Y$_2$Cl$_3$ are illustrated in Fig. 4 to further uncover their electronic properties. Through analysis of the partial charges, one can unambiguously understand the bonding character of the electrons in specified bands and the band distributions of the anionic electrons. There are invariably three bands observed around the Fermi level (denoted as band 1, band 2, and band 3) in YCl (Fig. 4a) and Y$_2$Cl$_3$ (Fig. 4b). These bands are closely related to the multiple metal–metal bonding in the shared-edge of the R$_6$ octahedrons (Fig. 4c), which are attributed to the stretched octahedral configurations. Such multiple metal–metal bonds can usually be observed in the heavier transition metal elements, e.g., Re–Re, Mo–Mo, and W–W. The unique divalent yttrium and scandium (Y$^{3+}$: 4$d^5$5$s^2$ and Sc$^{3+}$: 3$d^44$s$^2$) give rise to the formation of multiple Y–Y bonds, which has not been observed in most rare earth-containing compounds (no d electrons in R$^{4+}$). The partial charge density of band 1 in Y$_2$Cl$_3$ is shown in Fig. 4d; two lobes of atomic orbitals (d$_{z^2}$) in the Y atoms form a Y–Y π bonding within the nearest Y atoms. A similar case can be observed in the partial charge density of band 2 (Fig. 4e), where the Y–d$_{xy}$ orbitals of the nearest Y atoms develop another Y–Y π bonding. Besides, the Y–d$_{yz}$ orbitals (band 2) strongly overlap in the Y$_4$ tetrahedra forming a localized electron center, which is responsible for the presence of ELF attractors in R$_6$ tetrahedra. Decomposed Y-δ orbitals also show that the contributions from Y–d$_{xy}$ and Y–d$_{yz}$ are much stronger than other Y–d orbitals in the corresponding energy range of band 1 and band 2. The partial charge density of band 3 in YCl and Y$_2$Cl$_3$ are displayed in Fig. 4f, g, respectively. In sharp contrast with band 1 and band 2, the electrons in band 3 are loosely dispersed in the interstitial voids of the Y$_6$ octahedron layers (YCl) and chains (Y$_2$Cl$_3$), these electrons correspond to the ELF attractors in R$_6$ octahedron, which is a characteristic of electrides. The electrons in band 3 originated from the Y-5s orbital (Y: 4$d^7$5$s^2$ convert to t$_{2g}^2$: 4$d^4$5$s^2$, one electron in Y-Si orbital transferred to Cl-3p orbital, another is dispersed in the interstitial spaces) and two excess Y-5s electrons are available in their primitive cells. These electrons are confined in the interstitial spaces of the R$_6$ layers and chains, thus, band 3 can be described as ‘an interstitial band’. Oxygen atoms have been added into the center of the R$_8$ octahedron in YCl and Y$_2$Cl$_3$, as shown in Fig. 5a, b, and the band 3 disappears, suggesting that it does not belong to any specific atomic orbital but an interstitial site. To identify the contributions of interstitial electrons, the PDOS of the interstitial electrons in Y$_2$Cl$_3$ are plotted in Fig. 4c. The PDOS curves of the interstitial electrons are derived by adding a pseudatom with a Wigner–Seitz radius of 1.72 Å in the center of the octahedra. At the corresponding energy range of band 3, the contribution from interstitial electrons is larger than that of Y atoms. Since the size of the interstitial spaces is not large, the interstitial electron states are partially projected onto the Y–d orbitals (dominantly d$^2$) of the neighboring Y atoms, behaving like pseudo-σ bonds (denoted σ'). Band structure calculations reveal that YCl is ferromagnetic with a magnetic moment of 1.58 μ$_B$ per unit cell (2YCl per formula unit). Y$_2$Cl$_3$ is a semiconductor with a calculated band gap of 0.77 eV, and no spin polarization was observed. The magnetic properties (YCl) and semiconducting behavior (Y$_2$Cl$_3$) can be understood by detailed band structure analysis. The band 1 and band 2 in Y$_2$Cl$_3$ are fully occupied by the rest of d electrons (Y$^{3+}$: 4$d^5$5$s^2$, four d electrons available in primitive cell Y$_2$Cl$_3$), which are attributed to the diamagnetic and semiconducting character. For YCl, analogous to Y$_2$Cl$_3$, band 1 and band 2 are contributed by two Y–Y π bonding. However, only two d electrons are available in the primitive cell YCl and result in the high-spin state, which leads to the ferromagnetic character with a magnetic moment of 1.58 μ$_B$.

The band structures and partial charge density of the interstitial bands in ScCl, Sc$_2$Cl$_6$, and Sc$_7$Cl$_{10}$ are illustrated in Fig. S2a, b, c. The band structure with a magnetic moment of 1.53, 0.83, and 1.11 μ$_B$ per unit cell is predicted for ScCl, Sc$_2$Cl$_6$, and Sc$_7$Cl$_{10}$, respectively. For Sc$_2$Cl$_6$ (Fig. S2c), due to the double-chain configuration, four Sc–Sc π bands (two Sc–d$_{xy}$ and two Sc–d$_{yz}$) are observed.
Fig. 3  The electron localization function (ELF) of (a) YCl, (b) Y\textsubscript{2}Cl\textsubscript{3}, and (c) Sc\textsubscript{2}Cl\textsubscript{10}. The isosurface value was set as 0.75, 0.75, and 0.7, respectively. The ELF attractors located at the center of the \(R\textsubscript{4}\) tetrahedra (site A) and the \(R\textsubscript{6}\) octahedra (site B) are highlighted by blue and red circles. The ELF contours in the \(R\textsubscript{–}\text{Cl}\) layer (guided by red dashed line in the host structures) illustrated in the (1 1 0), (2 0 1), and (2 0 1) planes are shown at the bottom.

Fig. 4  Band structures for (a) YCl and (b) Y\textsubscript{2}Cl\textsubscript{3}. Spin-polarized calculations are included. There are three invariable bands in YCl and Y\textsubscript{2}Cl\textsubscript{3} around the Fermi level, which are denoted as band 1, band 2, and band 3. (c) The TDOS, PDOS curves, and Y–d orbitals in Y\textsubscript{2}Cl\textsubscript{3}, the bands where the anionic electrons confined are marked by 'inter' and green curves in band structure. (d) Orbital energy of multiple metal–metal bonding. Partial charge density of band 1, band 2, and band 3 are inserted. Partial charge density of band 3 in (g) YCl and (h) Y\textsubscript{2}Cl\textsubscript{3}, the partial charge density maps in (1 1 0) and (2 2 7) planes are inserted, the white line between nearest Y atoms are the guide for the shared edge of nearest \(Y\textsubscript{6}\) octahedron.
appear in the band structure, which leads to a magnetic moment of 1.11 \( \mu_B \) per unit cell (seven Sc-3d electrons are available in the primitive cell). Similar to YCl and \( \text{Y}_2\text{Cl}_3 \), the partial charge (green curves in the band structure) suggests that the interstitial electrons are loosely dispersed in the \( R_6 \) metal layer or chains, which is a characteristic of electrides. The PDOS of ScCl, Sc\(_5\)Cl\(_8\), and Sc\(_7\)Cl\(_{10}\) were also calculated through adding a pseudoatom (Wigner–Seitz radius was set as 1.65 Å in YCl, 1.61 Å in Sc\(_5\)Cl\(_8\), and 1.61 Å in Sc\(_7\)Cl\(_{10}\)) into the interstitial sites.\(^{20,34,64}\) It can be observed that, as plotted in Fig. S3a, b, c, the contributions of interstitial electrons are higher than those of Sc-\( d \)-orbitals in the energy range where interstitial bands are distributed.

Experimental characterization has also verified the semiconducting behavior of \( \text{Y}_2\text{Cl}_3 \). As shown in Fig. S4a, b, c, a band gap of 1.14 eV for \( \text{Y}_2\text{Cl}_3 \) can be estimated (Fig. S4b). Moreover, consistent with our calculations, the magnetic measurements of the \( \text{Y}_2\text{Cl}_3 \) sample suggest its diamagnetic nature, which is significantly different from the other reduced rare-earth chlorides discussed above.

Electronic dimensionality of interstitial electrons

The distributions of the anionic electrons and the interaction between them or other atoms can significantly influence the physical and chemical properties of electrides. For YCl and ScCl, the layer-like anionic electrons show up in the inner layer of the Cl–Y–Cl layers within the edge-sharing \( \text{Y}_6 \) octahedra (Fig. 5). This feature especially differs from those of typical \( A_3B \)-type 2D electrides,\(^{24}\) where the interstitial spaces appear between the \( A_3B \) layers. Flat bands are observed along the \( L-A, \Gamma-Z, \) and \( F-B \) orientations of the interstitial bands in the band structure, which corresponds to the directions perpendicular to the Cl–Y–Cl layers. The band dispersion is relatively smaller along the other directions and the anionic electrons are well confined in the 2D inner layer induced by the edge-sharing \( R_6 \) octahedrons, giving rise to a typical 2D electrode.\(^{16,25,65}\) \( \text{YCl}, \text{ScCl}_2, \text{Sc}_3\text{Cl}_6, \) and \( \text{Sc}_7\text{Cl}_{10} \) have similar channel voids where the anionic electrons are confined, and the interactions between the nearest anionic electrons are quite similar. The electrons confined in the metal octahedrons are weakly bonded with each other (Figs. 4h and S2b, c), and the connected anionic electrons forming 1D chains along the \( b \)-axis are reminiscent of previously reported 1D electrides.\(^{33,35,59}\) Thus, YCl and ScCl can be regarded as quasi-2D electrides with chemical formula of \([\text{YCl}]^\bigcdot \text{e}^- \) and \([\text{ScCl}]^\bigcdot \text{e}^- \); \( \text{Y}_2\text{Cl}_3, \text{Sc}_3\text{Cl}_6, \) and \( \text{Sc}_7\text{Cl}_{10} \) can be regarded as quasi-1D electrides with a chemical formula of \([\text{Y}_2\text{Cl}_3]^\bigcdot \text{e}^- \), \([\text{Sc}_3\text{Cl}_6]^\bigcdot \text{2e}^- \), and \([\text{Sc}_7\text{Cl}_{10}]^\bigcdot \text{4e}^- \) electrides.

Hydrogen absorption behavior

Typical electrides usually possess a strong hydrogen affinity caused by the effective interactions between the anionic electrons and hydrogen nuclei.\(^{35,66}\) The insertion of hydrogen atoms usually occupies the positions where the anionic electrons are trapped and induces a pronounced effect on the electronic properties of electrode materials. For example, hydrogen insertion makes the electrides transform to conventional ionic compounds, e.g., \( \text{C}_{12}\text{A}_7; \text{H}^\bigcdot\\text{A}^\bigcdot \text{H} \). It was also revealed that hydrogen permeation results in the 

\[ \text{RHal} \] 

(\( \text{R} = \text{Sc}, \text{Y}, \text{La, Ce, Pr, Nd, Gd, Tb, and Ho, } \text{Hal} = \text{Cl} \) and \( \text{Br}, x < ~1.0 \)).\(^{67,68}\) A similar observation was also reported in \( \text{Y}_2\text{Cl}_3 \).\(^{69}\) However, neutron diffraction studies suggest that hydrogen prefers to occupy the center of metal tetrahedrons instead of the \( R_6 \) octahedron.

To locate the position and investigate the influence of hydrogen on the yttrium and scandium chlorides electrides, YClH and \( \text{Y}_2\text{Cl}_3\text{H} \) were constructed with hydrogen atoms located in the center of the metal tetrahedrons (crystallographic 6c site for YCl and 4i site for \( \text{Y}_2\text{Cl}_3 \)). Hydrogen atoms were also added in the center of the metal octahedron; however, the imaginary phonon frequency modes confirm the loss of structural integrity with H entry into the octahedron site of YCl and \( \text{Y}_2\text{Cl}_3 \) (see Fig. S5a, b), which concurs with the experimental observation. The calculated band structures of YClH (Fig. 6a) and \( \text{Y}_2\text{Cl}_3\text{H} \) (Fig. 6b) show that the introduction of the H atom leads to Fermi level reorganization. Although the H atom has been added into the center of the metal tetrahedron, band 3, where the anionic electrons are mainly confined, vanished in both YCl and \( \text{Y}_2\text{Cl}_3 \) transforming to a conventional ionic crystal. The interstitial electrons in band 3 are found to transfer to the H 1 s orbital caused by the strong hydrogen affinity of the interstitial electrons. Since the Y–Y \( \pi \) bonding (\( d_{yz} \), band 2 in YCl, and \( \text{Y}_2\text{Cl}_3 \)) formed electron maxima in the \( R_6 \) tetrahedron, the repulsion...
between $H^-$ ($1s^2$) ions and electrons in $R_4$ tetrahedron significantly increases the energy of this $Y-Y$ π bonding, which is responsible for the Fermi level reorganization. For YClH, the electrons in band 2 of YCl are transferred to another $Y-Y$ π bonding (band 1 in YCl, $d_{yz}$), which leads band 1 to shift to the valence region in YClH (green curves in Fig. 6a), and no spin polarization was confirmed after hydrogen insertion. Due to the band 1 in Y$_2$Cl$_3$ being fully occupied by two Y-4$d$ electrons, Y$_2$Cl$_3$H is unperturbed in Fig. 6b (green curves) and the electrons in the $Y-Y$ π bonding of $d_{yz}$ orbital move to the conduction band region, resulting in the significant transition from semiconductor to metal.

The intriguing locations of the H atoms drive the electrons in band 2 to transfer to other bands in a higher energy region, which significantly increases the energy at the Fermi level (1.0 and 0.42 eV higher than YCl and Y$_2$Cl$_3$, respectively, Fig. 6a, b). Such unusual variation may induce significant modification of work function (WF) ($\Phi_{WF}$). Thus, the WFs of YCl, Y$_2$Cl$_3$, YClH, and Y$_2$Cl$_3$H were calculated. The most stable surfaces are the [0 0 1] planes for YCl and YClH, and the [2 0 1] planes for Y$_2$Cl$_3$ and Y$_2$Cl$_3$H. As illustrated in Fig. 5a, b, c, d, the WFs show strong anisotropic characters for these phases, similar to the typical electrides with layered structural configuration, e.g. Y$_2$C$_2$O$_4$ and Ca$_2$N$_2$.71 For YClH, the calculated WF of the [1 1 0] plane decreases to 2.47 eV (3.13 eV in YCl). However, the WF of the [0 1 0] planes for Y$_2$Cl$_3$H remains largely unchanged (2.81 and 2.94 eV in Y$_2$Cl$_3$ and Y$_2$Cl$_3$H). Considering the layered-like structure in the host structures, these surfaces parallel to the $Y-Cl$ layers tend to be exposed. YClH$_{0.5}$ with H partially occupying the center of the $R_4$ tetrahedron was constructed to study the effect of hydrogen. As shown in Fig. S7, band 3 remains, suggesting that YClH$_{0.5}$ retains its electride nature after hydrogen absorption. The Fermi level also increased by 0.12 eV, leading to the decrease of WFs in the [0 0 1] planes. The increased energy at the Fermi level, the insertion of hydrogen atoms results in a sharp decrease of WFs; 4.57 and 3.40 eV along the [0 0 1] planes for YCl (Fig. 6c) and YClH (Fig. 6e), and 3.75 eV (relative to CBM), 3.20 eV along the [0 0 1] planes for Y$_2$Cl$_3$ (Fig. 6d) and Y$_2$Cl$_3$H (Fig. 6f), respectively. Surfaces with orientations perpendicular to the $Y-Cl$ layers were also calculated in [1 1 0] of YCl and YClH, and [0 1 0] for Y$_2$Cl$_3$ and Y$_2$Cl$_3$H. As illustrated in Fig. 5a, b, c, d, the WFs show strong anisotropic characters for these phases, similar to the typical electrides with layered structural configuration, e.g. Y$_2$C$_2$O$_4$ and Ca$_2$N$_2$.71 For YClH, the calculated WF of the [1 1 0] plane decreases to 2.47 eV (3.13 eV in YCl). However, the WF of the [0 1 0] planes for Y$_2$Cl$_3$H remains largely unchanged (2.81 and 2.94 eV in Y$_2$Cl$_3$ and Y$_2$Cl$_3$H). Considering the layered-like structure in the host structures, these surfaces parallel to the $Y-Cl$ layers tend to be exposed. YClH$_{0.5}$ with H partially occupying the center of the $R_4$ tetrahedron was constructed to study the effect of hydrogen. As shown in Fig. S7, band 3 remains, suggesting that YClH$_{0.5}$ retains its electride nature after hydrogen absorption. The Fermi level also increased by 0.12 eV, leading to the decrease of WFs in the [0 0 1] planes. The

Fig. 6 Band structures and work functions for YClH (a, c, e) and Y$_2$Cl$_3$H (b, d, f). a, b Band structures. c, e, d, f Calculated work functions as a function of position (Å) along c-axis for YCl and YClH in the (0 0 1) surfaces, Y$_2$Cl$_3$ and Y$_2$Cl$_3$H in the (0 1 0) surfaces. The Fermi level is set as 0 eV, the Fermi level in YCl and Y$_2$Cl$_3$ is also marked by a black line in the band structures. The green curves are the band 1 in YCl and Y$_2$Cl$_3$ which remains after H absorption. The bands contributed by hydrogen atoms are marked by red curves.
decreased WF after hydrogen absorption found in YCl and Y₂Cl₃ is opposite to typical electrides, which may lead to a new chemical and physical understanding of electrides.

Extending to LaCl
We also extended our study to lanthanide halide because the lanthanide elements usually possess similar chemical properties. LaCl takes the same crystal structure as YCl, but the band structures accompanied with an ELF and partial charge density of LaCl and LaClH (H located in the La₄ tetrahedron) are displayed in Fig. S8a, b. Similar to YCl, the partial charge density of the interstitial bands (green curves in the band structure) suggest that the interstitial electrons exist in the center of the La₄ octahedron, to form layer-like anionic electrons in the inner layer of the Cl-La-La-Cl layers, suggesting its 2D electride character. For LaClH, the variation of the Fermi level also lead to decreased WF in the [0 0 1] (from 2.81 eV in LaCl to 3.54 eV in LaClH) and [1 1 0] (from 4.51 eV in LaCl to 3.45 eV in LaClH) and [1 1 0] (from 2.81 eV in LaCl to 3.54 eV in LaClH) directions, suggesting its 2D electride character. For LaClH, the variation of the Fermi level also lead to decreased WF in the [0 0 1] (from 2.81 eV in LaCl to 3.54 eV in LaClH) and [1 1 0] (from 4.51 eV in LaCl to 3.45 eV in LaClH) and [1 1 0] (from 2.81 eV in LaCl to 3.54 eV in LaClH) directions, suggesting its 2D electride character.

METHODS
The rare-earth chlorides were selected from the Materials Project platforms and ICSD. The structural relaxations and calculations were performed using the density functional theory (DFT) as implemented in the Vienna Ab initio simulation package (VASP) within the projector-augmented-wave (PAW) method. Generalized-gradient approximation (GGA-PBE) was used for the electron exchange–correlation interaction. The PAW potentials valence electrons of Y as 4s², 4p⁶, 5d⁴, 6s² as 3p⁶, 3d³, 4s⁴, 5s and Cl as 2s², 2p⁶ were adopted. The plane-wave kinetic energy cutoffs were set to be 600 eV, and a dense Brillouin zone sampling grid with a resolution of 2π/0.03 Å⁻¹ was chosen to ensure the enthalpy calculations converged well within 1 meV/atom. Spin-polarized calculations were considered.

To determine the WF (ΦWF) of YCl and Y₂Cl₃, we constructed two slab models of [0 0 1] (24 atoms) and [1 1 0] (48 atoms) crystal planes for YCl, and [0 1 0] (90 atoms) and [2 0 1] (50 atoms) crystal planes for Y₂Cl₃, which are perpendicular or parallel to the edge-sharing metal octahedron chains (YCl₄) and layer (YCl). The vacuum was set as 25 Å for those slab models. The k-point grids were set as 15 × 15 × 1 and 8 × 5 × 1 for the [0 0 1] and [1 1 0] crystal planes of YCl, and 5 × 4 × 1 and 5 × 13 × 1 for the [0 0 1] and [2 0 1] crystal planes for Y₂Cl₃ using the Monkhorst–Pack method. A similar set-up was applied to the YClH and Y₂Cl₄ hydrides. The ΦWF value was determined using the equation: ΦWF = E_F∞C − E_F0, where E_F∞C is the vacuum level, and E_F0 is the Fermi level. The crystal structure, ELF, and charge density maps were made by VESTA.

The samples used in the measurements were synthesized using a conventional solid-state reaction. The elemental yttrium (turning) and YCl₃ (powder) were mixed with the ratio of Y:YCl₃ = 1:1 and sealed into an Ar-filled tube. The tube was sintered twice at 750 °C for 48 h to ensure homogeneity. The obtained powders were then filtered to exclude excess yttrium. The obtained samples were black in color and sensitive to air. Powder XRD patterns were collected on a Bruker D8 advance diffractometer with CuKα radiation at room temperature. To avoid air exposure, the samples were sealed into the plastic sample holder filled with Ar gas.

The optical reflectance was measured using a UV–visible spectrophotometer (Hitachi U-4000) at room temperature. The samples were pelletized and sealed into an Ar-filled sample holder during the measurements to avoid air exposure. The magnetic properties were measured using commercial SSVM (Quantum design). LaClH₆.₆ was synthesized by solid-state reaction from La metal, LaH₃, and LaCl₃. LaH₃ was obtained by heating metal La in a H₂ atmosphere. All starting materials and precursors were prepared in a glove box under a purified Ar atmosphere. The mixture of starting materials was wrapped with Mo foil and placed in the sealed stainless tube; the tube was heated at 973 K for 36 h. The amount of hydrogen incorporated in LaClH₆.₆ was measured by TDS (ESCO TDS-1000S/W). The WF of LaClH₆.₆ was determined from a cut-off energy of ultraviolet photoemission spectroscopy (UPS, hv: 21.2 eV) spectra. Clean surface was prepared by cleaving the LaClH₆.₆ bulk sample in the glove box that is directly connected to the UPS chamber. DC bias dependence was also checked at 5, 7, and 10 V.

DATA AVAILABILITY
The data that support the findings of this study are available from the corresponding authors, Professor Huiyang Gou of the Center for High Pressure Science and Technology Advanced Research (email: huiyang.gou@hpstar.ac.cn) and Professor Hideo Hosono of Materials Research Center for Element Strategy, Tokyo Institute of Technology (email: hosono@msl.titech.ac.jp) upon reasonable request.

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