A polarity-induced defect mechanism for conductivity and magnetism at polar–nonpolar oxide interfaces

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The discovery of conductivity and magnetism at the polar–nonpolar interfaces of insulating nonmagnetic oxides such as LaAlO₃ and SrTiO₃ has raised prospects for attaining interfacial functionalities absent in the component materials. Yet, the microscopic origin of such emergent phenomena remains unclear, posing obstacles to design of improved functionalities. Here we present first principles calculations of electronic and defect properties of LaAlO₃/SrTiO₃ interfaces and reveal a unifying mechanism for the origins of both conductivity and magnetism. We demonstrate that the polar discontinuity across the interface triggers thermodynamically the spontaneous formation of certain defects that in turn cancel the polar field induced by the polar discontinuity. The ionization of the spontaneously formed surface oxygen vacancy defects leads to interface conductivity, whereas the unionized Ti-on-Al antisite defects lead to interface magnetism. The proposed mechanism suggests practical design principles for inducing and controlling both conductivity and magnetism at general polar–nonpolar interfaces.
Oxide interfaces exhibit many spectacular phenomena not found in the respective bulk components or in conventional semiconductor interfaces\(^1\), providing new avenues for electronics\(^2\). The LaAlO\(_3\)/SrTiO\(_3\) interface is a paradigm example, exhibiting conduction two-dimensional (2D) electron gas (2DEG)\(^3\) and magnetism\(^4\)–\(^11\) between two insulating nonmagnetic metal oxides. In the [001] direction, two different interfaces can be formed between polar LaAlO\(_3\), which consists of alternating LaO\(^+\)–(AlO\(_2\))\(^-\) layers, and nonpolar SrTiO\(_3\), which consists of alternating (SrO)\(^0\)–(TiO\(_2\))\(^0\) layers. One is LaO/TiO\(_2\) stacking configuration (so-called n-type) and the other is AlO/SrO configuration (so-called p-type). The remarkable feature is that the conductivity occurs only at n-type interfaces when the LaAlO\(_3\) film thickness (\(n_{\text{LAO}}\)) is larger than three unit cells (uc)\(^6\), whereas the magnetism has been observed both at n-type interfaces with \(n_{\text{LAO}} \sim 3\) uc and at insulating p-type interfaces\(^8\). Table 1 lists some experimental observations representing the main puzzles\(^12\) that need to be resolved before the promised applications can be realized\(^13\).

For 2DEG at n-type interfaces, four main mechanisms have been suggested, yet no single one explains the full scope of these puzzles. The prevalent one is intrinsic electronic reconstruction (so-called polar catastrophe) involving ionization of the electrons from host valence band of LaAlO\(_3\) within the abrupt and defect-free interfaces (Supplementary Fig. 1)\(^3\). The other three mechanisms involve various defects, including the oxygen vacancies at the interface (denoted as \(V_{\text{O}(\ell)}\), where \(\ell\) means ‘Interface’)\(^14\)–\(^16\), oxygen vacancies at LaAlO\(_3\) overlayer surface (denoted as \(V_{\text{O}(S)}\), where \(S\) means ‘Surface’)\(^17\)–\(^22\), and the La-on-Sr (LaSr) antisite donor defects induced by interfacial cation intermixing\(^23\)–\(^29\). As Table 1 shows, each of these proposed mechanisms represents one aspect of the interface physics, explains some experimental findings, but conflicts with a few others\(^2\). None explains the insulating nature of n-type interfaces. Regarding interface magnetism, it was shown experimentally that the local magnetic moments are associated with Ti\(^{3+}\) ions\(^5\)–\(^11\),\(^30\). However, it is yet unclear whether such Ti\(^{3+}\) ions reside in the interface within SrTiO\(_3\), or LaAlO\(_3\), or both sides. Theoretically, it has been argued that the Ti\(^{3+}\) ions arise in SrTiO\(_3\) side, owing to the occupation of the low-energy Ti-\(d_{xy}\)-like sub-bands caused by the interfacial splitting of orbital degeneracy\(^31\), or interfacial disorder\(^32\),\(^33\), or interfacial oxygen vacancies\(^34\). However, these scenarios are difficult to explain the fact that magnetism occurs at p-type interfaces and n-type interfaces with a critical thickness (\(L_c\)) similar to that for 2DEG.

The centrosymmetric III–III–O\(_3\) perovskite has a non-zero formal polarization, as established by the modern theory of polarization\(^35\),\(^36\). The discontinuity in the formal polarization of LaAlO\(_3\) and SrTiO\(_3\) leads to a finite polar field that would cause the divergence of electrostatic potential as the \(n_{\text{LAO}}\) increases. A crucial issue associated with the emergent conductivity and magnetism at polar–nonpolar interfaces is what mitigates such potential divergence. Is it electronic reconstruction within the polar catastrophe scenario, or the atomic reconstruction scenario with or without chemical defects? Different mechanisms suggest different experimental designs that would control conductivity, mobility and magnetism. Particularly, for defects, it is unclear which defects can be induced and are responsible for the emergence interface phenomena. Using first principles electronic and defect calculations, we find that the certain defects would form spontaneously in response to the built-in polar field. The ensuing polarity-induced defect mechanism (Fig. 1) simultaneously explains the main features of both conductivity and magnetism at the interface, as summarized in Table 2.

The key defect-related physical quantities that feature in our explanation are (i) the formation energy \(\Delta H\) of defects in various charge states \((q)\) at the thermodynamic equilibrium Fermi energy \(E_F\) (Fig. 2). This \(\Delta H\) controls the equilibrium defect concentration; (ii) the defect charge transition energy levels (deep or shallow; Fig. 3); \((q/q')\) defined as the \(E_F\) where the \(\Delta H\) of a defect in two different charge states \(q\) and \(q'\) equal. A donor can produce electrons and compensate holes, whereas an acceptor can produce holes and compensate electrons. These two quantities (i) and (ii) calculated for charged defects located in different layers across the interfaces turn out to be crucial. The details of their first principles calculations are given in the Methods section.

The central point of the proposed mechanism is that the polar-discontinuity-induced built-in polar field triggers thermo dynamically the spontaneous formation of certain defects at the surface and/or interface, which in turn compensate the built-in polar field and thus avoids the potential divergence. Thus, it is the polar-field-induced defects, rather than the electronic or atomic reconstruction, that are responsible for the conductivity and magnetism at the interface. Specifically, we find that the surface \(V_{\text{O}}\) has its donor levels located energetically above the SrTiO\(_3\) conduction band at the interface but below the LaAlO\(_3\) conduction band. This donor level position is a prerequisite for 2DEG formation. Although the occurring of the 2DEG is because of the surface donors, the density of 2DEG is controlled by the interfacial deep acceptor defects (mainly Al-on-Ti antisite). It has also turned out that the interface magnetic moment is caused by the unionized deep Ti-on-Al antisite defects located within the LaAlO\(_3\) side near the interface.

We address below how this polar-field-induced defect mechanism resolves the long-standing puzzles on the origin of 2DEG, the critical thickness for 2DEG, the weak field in LaAlO\(_3\), and SrTiO\(_3\).

Table 1 | List of some important experimental observations at LaAlO\(_3\)/SrTiO\(_3\) interfaces.

| Interface structure | Experimental observations | Polar catastrophe | Cation mixing | \(V_{\text{O}}\) at interface | \(V_{\text{O}}\) at surface | Current mechanism |
|---------------------|--------------------------|-------------------|--------------|-----------------------------|----------------------|------------------|
| n-type              | Critical thickness \((L_c) = 4\) uc | ✓         | X           | ✓                          |          | ✓                |
|                     | 2DEG density < 0.5e \(\text{uc}^{-1}\) |          |             | ✓                          |          | ✓                |
|                     | Weak \(E_F\) in LaAlO\(_3\) for \(n_{\text{LAO}} < L_c\) |          |             | X                          |          | ✓                |
|                     | Weak \(E_F\) in LaAlO\(_3\) for \(n_{\text{LAO}} \geq L_c\) |          |             | X                          |          | ✓                |
|                     | LaAlO\(_3\) surface: insulating |          |             | ✓                          |          | ✓                |
|                     | Interface: cation intermixed |          |             | X                          |          | ✓                |
|                     | Interface magnetism |          |             | X                          |          | ✓                |
| p-type              | Interface: insulating |          |             | X                          |          | ✓                |
|                     | LaAlO\(_3\) surface: insulating |          |             | X                          |          | ✓                |
|                     | Interface: cation mixed |          |             | X                          |          | ✓                |
|                     | Interface magnetism |          |             | X                          |          | ✓                |

The symbol of ✓ and X mean that the mechanism agrees or disagrees, respectively, with the experimental observation. The ‘^\_’ symbol denotes uncertainty.
film, the density of 2DEG, the insulating nature of p-type interfaces and the origin of the local magnetic moments. During this process, we also distil the general design principles that control the pertinent effects and could allow future section of better polar–nonpolar interface materials.

**Results**

**The origin of the 2DEG.** The 2DEG is unlikely to originate from the defect-free scenarios: these include the ionization of the intrinsic LaAlO3 valence bands (suggested by the polar catastrophe model18-20) or the ionization of the LaO interface layer (suggested by the interfacial charge-leaking model21 (Supplementary Note 1). This conclusion stems from the fact that the creation of 2DEG in these defect-free scenarios requires the LaAlO3 valence band maximum (VBM) to cross the SrTiO3 conduction band minimum (CBM) or E_F. However, this is contrary to the experimentally observed weak field (negligible band-bending)38-41 in the LaAlO3 film, clearly showing that the LaAlO3 VBM is located energetically far below E_F.

The 2DEG also is unlikely to originate from interfacial point donor defects (LaSr, TiAl and V0). Recall that the defect formation energy (ΔH) depends on the E_F (or chemical potential) and the defect charge transition energy (Δq) needs to be close to band edges in order to produce free carriers. In thermodynamic equilibrium, the E_F of the system pins around the middle of the SrTiO3 band gap when n_{LaO} < L_c and around the SrTiO3 conduction band edge near the interface when n_{LaO} ≥ L_c (Supplementary Note 2). In either case, Fig. 2ab shows that the ΔH of the interfacial antisite donor defects, La0 and Ti0, is small positive or even negative (note: the superscript denotes the defect charge state, not the nominal oxidation state of the atom at the interface). In other words, the formation of such antisite defects at the thermodynamic equilibrium E_F is energetically favourable and would inevitably lead to interfacial cation mixing. However, at such E_F, both La0 and Ti0 defects are stable in their charge neutral states (as indicated by the superscript), contributing no free carriers. On the other hand, the interfacial VO defects are energetically stable in the charged states, that is, V2+ (Fig. 2a,b). This means that, if formed, the VO will donate electrons and thereby become positively charged. However, the ΔH of V2+ at such equilibrium E_F is rather high (> 2.5 eV), implying that V2+ have very low concentration under thermodynamic equilibrium conditions. The high ΔH also means that even if the VO defects are formed under nonequilibrium growth conditions, they can still be removed easily by the post-O-rich annealing process42 (Supplementary Note 3). Thus, contrary to earlier postulations, these interfacial donor defects are not responsible for 2DEG, consistent with recent experiments43.

![Figure 1](image1.png) Schematic band diagram and change transfer among the defects at LaAlO3/SrTiO3 interfaces. (a) n-type interfaces with n_{LaO} < L_c: all electrons transferred from TiAl(S) are trapped by deep A1(T)l, causing no 2DEG. (b) n-type interfaces with n_{LaO} ≥ L_c: VO(S) defects donate ~ 0.5 e S2-1 to the interface. Part of ~ 0.5 e S2-1 is trapped by the A1(T)l and the rest leads to interfacial 2DEG. The formed TiAl defects are ionized, i.e., Ti3+ on Al3+, having local magnetic moments. (c,d) p-type interfaces with n_{LaO} < L_c (~ 4 uc) and n_{LaO} ≥ L_c; all electrons transferred from La0 are trapped by Sr0(S) and V0(S), respectively. All involved defects are deep and do not induce carriers. The un-ionized Ti0 in (c,d) also form and induce local moments. The superscripts (0, +, ++, −) in the figure denote the defect charge states, not the oxidation states of the ions there.

![Figure 2](image2.png) Formation energy of the interfacial point defects at thermodynamical equilibrium Fermi energy. (a,b) n-type interfaces with n_{LaO} < L_c and n_{LaO} ≥ L_c, respectively. (c) p-type interfaces. At a given E_F, the defect in different charge states (for example, V0, V0−, V0+) usually has different ΔH and the only one with the lowest ΔH is shown in the figure. The ΔH versus E_F for these defects are shown in Supplementary Fig. 2, which also includes other high-ΔH defects not shown here. The chemical potentials for Sr, Ti, La, and AlO are ~ 4.36, ~ 6.20, ~ 6.10, ~ 5.46 and ~ 2.0 eV, respectively, relative to their corresponding elemental solid or gas phases, which corresponds to T = 1050 K and P_{O2} = 6.1 × 10−6 Torr (Supplementary Fig. 3).
The oxygen vacancy, $V_O(S)$, at the free LaAlO$_3$ surface can explain the interfacial 2DEG. For this to happen, three conditions (‘design principles’) need to be satisfied. First, $V_O(S)$ in the polar film material needs to have a sufficiently low formation energy $\Delta H_f$; therefore, it could form in significant quantities. Figure 4a shows that the $\Delta H_f$ of $V_O(S)$ decreases linearly as the film thickness $n_{LAO}$ increases, consistent with previous calculations$^{20,44}$. When $n_{LAO} > 3$–4 uc, the $\Delta H_f$ becomes zero or negative, and $V_O(S)$ will form spontaneously. The large negative $\Delta H_f$ means that even exposing the surface to air or post annealing under O-rich environment cannot remove these vacancies. Second, the system needs to have a none-zero built-in polar field that would enable the electron to transfer from the surface of the polar material to the interface. Such transfer sets up an electric field that would enable the electron to transfer from the surface of the nonpolar material to the interface. This picture suggests that the 2DEG at n-type LaAlO$_3$/SrTiO$_3$ interfaces may also be induced and/or tuned by using certain surface adsorbates (for example, H$_2$O and H)$^{45–47}$ or metallic contactse$^{48}$ provided that the ionization energy of the surface adsorbate or the metallic contact is not lower than the donor level of the $V_O(S)$.

The origin of the critical thickness. The linear decrease in $\Delta H_f$ of $V_O(S)$ with increasing polar film thickness $n_{LAO}$ naturally explains the critical thickness $L_c$ for the metal–insulator transition. The calculated rate of decrease (that is, the slope $d\Delta H_f/dn_{LAO}$) equals 0.19 eV Å$^{-1}$, which is the same as the calculated built-in polar field in the defect-free LaAlO$_3$ film (Supplementary Note 4). The $V_O(S)$ defects start to form spontaneously when the $\Delta H_f$ becomes zero at the $L_c$ of ~4 uc under a typical O-rich growth condition (Fig. 4a). For the LaAlO$_3$ film that is 1 uc thinner than this $L_c$, the calculated $\Delta H_f$ of $V_O(S)$ is 0.75 eV, which is too high to produce significant free carrier concentration. Thus, the appearance of $V_O(S)$ (and the ensuing metal–insulator transition) at $L_c$ is predicted to be a sharp transition (Supplementary Note 5), distinct from the gradual appearance of 2DEG behaviour as predicted from polar catastrophe model, but consistent with experiments$^{39}$.

Figure 3a suggests that the $L_c$ resulting from $V_O(S)$ can be written as $L_c = \Delta H_f/eP_0$, where $\Delta H_f$ is the formation energy of the $V_O(S)$ at interface (or the $\Delta H_f$ extrapolated at $n_{LAO} = 0$) and $P_0$ is the built-in polar field. Using $E_P = 4\pi P_0/\epsilon$ (where $\epsilon$ and $P_0$ are the dielectric constant and formal polarization of LaAlO$_3$ film), this relation can be written as

$$L_c = \Delta H_f/4\pi \epsilon P_0$$  

(1)

which predicts an $L_c$ of ~4 uc, depending slightly on the O-poor/ rich growth conditions (Supplementary Note 6). The above formula provides an alternative explanation for the observed variation of the $L_c$ with the fraction $x$ in (LaAlO$_3$)$_{1-x}$(SrTiO$_3$)$_x$ overlayer (where $P_0$ is proportional to $x$)$^{50}$. This observation was originally explained by $L_c = \Delta \Phi/4\pi \epsilon P_0$ (where $\Delta \Phi$ is the energy difference between LaAlO$_3$, VBM and SrTiO$_3$ CBM) within polar catastrophe model$^{50}$. Since $\Delta \Phi$ and $\Delta H_f$ have accidentally similar value (~3–4 eV) in this system, it is not surprising that the $L_c$ predicted from these two models is also similar. However, the $V_O(S)$ model clearly explains many other observations in which the polar catastrophe model fails (Table 1).

Implication on the design of carrier mobility: (i) the relatively high 2DEG mobility could be enabled by a modulated doping effect$^{51}$, whereby the source of carriers (here at the LaAlO$_3$ surface) is spatially separated from the location where the carriers reside (here at the LaAlO$_3$/SrTiO$_3$ interface), thus minimizing carrier scattering by the ionized defects. This minimal spatial separation is measured by the critical thickness $L_c$. The equation (1) suggests that a large $L_c$ (hence maintaining good mobility) could be achieved by selecting a polar materials with small polarization, large dielectric constant and donor defects

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**Figure 3 | Charge transition energy levels of the interfacial point defects.**

(a) n-type interface. (b) p-type interface. The defect charge transition energy level is defined as the $E_T$ where the $\Delta H$ of a given defect in two different charge states equal. Some defects may have multiple charge transition energy levels. For example, $V_{Sr}$ has the two transition energy levels (one is for the transition between neutral charge state and $-$1, and the other is between $-$1 and $-$2). In such case, if the defect is donor (red), only the lowest level is shown, and if the defect is acceptor (blue), the highest level is shown.
Polar field compensation. Experimentally, only very weak residual field has been observed in the LaAlO$_3$ film no matter whether its thickness is below or above the $L_c$ (refs 38–41,52). This observation cannot be explained within the defect-free interface scenario, even including the ionic relaxations$^{33}$. In turn, whereas the $V_O(S)$ model explains the weak electric field in LaAlO$_3$ film above the $L_c$, it does not explain it below the $L_c$. This leads us to inspect the effects of all possible cation antisite defects across the interface.

Each individual interfacial antisite alone cannot cancel the polar field. Figure 2ab shows that the $\Delta V_O(\text{Sr})$, $\Delta V_O(\text{Ti})$, $\Delta V_O(\text{Sr})$ and $\Delta V_O(\text{Ti})$ antisite defects have lower $\Delta H$ than other point defects (for example, cation vacancies) in the layer where they are located. Therefore, the former are the dominant defects in their corresponding layers. The interfacial SrLa donor in the SrTiO$_3$ side cannot set up an opposite dipole across the LaAlO$_3$ film that can cancel the polar field inside the LaAlO$_3$ film. Regarding the TiAl donor in the LaAlO$_3$ side, the donor level is lower than the SrTiO$_3$ conduction band at the interface. Therefore, the ionized electrons cannot be transferred to the latter so as to cancel the polar field. Regarding the interfacial Al$_{\text{Tf}}$ and Sr$_{\text{La}}$ acceptors, the polar field compensation is similar to that in the polar catastrophe model: before the LaAlO$_3$ VBM reaches the acceptor levels of Al$_{\text{Tf}}$ or Sr$_{\text{La}}$, the polar field cannot be cancelled.

The $[\text{TiAl}+\text{AlTi}]$ defect pair is the most potent source of polar field cancellation among those donor–acceptor antisite defect pairs at n-type interfaces. The four leading antisite defects can form four types of donor–acceptor pairs: $[\text{TiAl}+\text{AlTi}]$, $[\text{LaSr}+\text{SrLa}]$, $[\text{LaAl}+\text{AlTi}]$ and $[\text{TiAl}+\text{SrLa}]$, denoted as (i), (ii), (iii) and (iv), respectively, in Fig. 3. Clearly, the electron transfer from donor to acceptor in both pairs (i) and (ii) is unlikely since it will create a dipole in the same direction as the intrinsic dipole in LaAlO$_3$ and thus increase the dipole moment (also the electrostatic energy) and destabilize the interface. In pairs (iii) and (iv), the charge transfer can cancel the polar field. However, the electron transfer in pair (i) is energetically much more favourable because, first, Al$_{\text{Tf}}$ has a lower acceptor level than Sr$_{\text{La}}$ and, second, the donor–acceptor separation distance (also the associated opposite dipole moment that lowers the total energy of the system) is larger in pair (i) (Fig. 3a). We thus next focus on $[\text{TiAl}+\text{AlTi}]$ (that is, pair (iv)). For $n_{\text{LAO}} \geq L_c$, the $[\text{AlTi}+\text{TiAl}]$ antisite pair can form spontaneously via Ti $\leftrightarrow$ Al exchange across the interface and cancel the polar field. Figure 4b (filled symbols) shows that the energy required to form such defect pair is negative (that is, exothermic), and the largest energy gain is obtained when a Ti atom at the TiO$_2$-interface monolayer is exchanged with an Al of the AlO$_2$-surface monolayer, that is, $\Delta H_D \approx 1.5$ eV (Supplementary Fig. 3a). (Fig. 4a) and $[\text{AlTi}+\text{TiAl}]$ pair (Fig. 4b) have zero or negative $\Delta H$, meaning that both could form in ideal interfaces. However, if both $V_O(\text{Sr})$ and $\text{TiAl}$ are present, since $V_O(\text{Sr})$ has an energetically higher donor level than TiAl (Fig. 3a), the $V_O(\text{Sr})$ would transfer electrons to the TiAl defects. The polar field that was initially cancelled by the electrons transferred from the TiAl defects are then released and get cancelled by the electrons transferred from $V_O(\text{Sr})$ defects. Consequently, the polar field in the whole LaAlO$_3$ film would be cancelled by the $V_O(\text{Sr})$ defects (if present). The larger the $n_{\text{LAO}}$ the lower the $\Delta H$ of the $V_O(\text{Sr})$. After the polar field has been cancelled by $V_O(\text{Sr})$, Fig. 4b (open symbols) shows that the $\Delta H$ of $[\text{AlTi}+\text{TiAl}]$ pair becomes positive (0.4–0.7 eV), meaning that $[\text{TiAl}+\text{AlTi}]$ pairs cannot be formed via Ti $\leftrightarrow$ Al exchange over a distance beyond $L_c$. In brief, the presence of the $[\text{TiAl}+\text{AlTi}]$ defect pairs in the sample does not change the linear-decreasing behaviour in the $\Delta H$ of the $V_O(\text{Sr})$ (Fig. 4a), suggesting that the metal–insulator transition still occurs at the $L_c$ of $\sim 4$ uc. However, the presence of $V_O(\text{Sr})$ would prevent $[\text{TiAl}+\text{AlTi}]$ pairs forming further above the $L_c$ and reduce the concentration of these pairs formed below the $L_c$. Having high $\Delta H$ at the interface or in the bulk. On the other hand, (ii) the concentration of interfacial defects must be minimized in order to take advantage of (i). In addition, (iii) since the 2DEG is located at the conduction bands of the nonpolar material, it is advantageous to select the nonpolar material with low electron effective mass in order to achieve higher mobility.
The density of the 2DEG. Reinterpretation of the puzzle: According to Gauss’ law, the experimentally observed weak electric field in LaAlO₃ film means that the total external charge density (mobile and/or immobile) at the interface must be \( \sim 0.5e \) \( S_{2D}^{-1} \) (Supplementary Note 7), as recently observed². For \( n_{LAO} < L_c \), there is no interfacial conductivity and thus none of these interfacial charge contribute to the conductivity. For \( n_{LAO} \geq L_c \), only a fraction of 0.5e \( S_{2D}^{-1} \) interfacial charge is seen in transport, and so the majority of 0.5e \( S_{2D}^{-1} \) charges do not contribute to the conductivity. The puzzle thus is why the \( \sim 0.5e \) \( S_{2D}^{-1} \) charge exists at the interface with any \( n_{LAO} \), but only a small part of it contributes to conducting 2DEG when \( n_{LAO} > L_c \).

This puzzle cannot be explained by defect-free polar catastrophe model³⁴ or interfacial charge-leaking model³⁳, since both predict zero interfacial charge for \( n_{LAO} < L_c \) and an interfacial charge density much higher than the measured 2DEG density for \( n_{LAO} \geq L_c \) (Supplementary Fig. 1). The possibility of ‘multiple carrier types’ at defect-free interfaces (that is, those electrons occupying interfacial \( d_{ox} \) sub-band and those occupying \( d_{ox}/d_{oz} \) sub-bands contributing differently in transport) has also been suggested to explain the measured 2DEG density (above the \( L_c \)) (refs 56–59). However, this scenario could not explain the total 0.5e \( S_{2D}^{-1} \) interface charge that is independent of \( n_{LAO} \). Moreover, it is also difficult to explain why a full carrier density of 0.5e \( S_{2D}^{-1} \) has been observed at GdTiO₃/SrTiO₃ interfaces (where the same multiple carrier types exist)⁶⁰.

The 2DEG density is controlled by the concentration of immobile acceptor defects that can trap itinerant electrons. Within the emerging defect picture, the total interfacial charge is always \( \sim 0.5e \) \( S_{2D}^{-1} \), which corresponds to the (almost) complete polaron field cancellation. In the SrTiO₃ side (where the 2DEG is located), there are mainly three types of acceptor defects, namely, \( Al_{Ti} \), \( VSr \), and \( VTi \). At equilibrium \( E_F \), Fig. 2a,b shows that these acceptor defects all prefer to stay in negative charge states, that is, \( Al_{Ti}^- \), \( VSr^- \), and \( VTi^- \). (In other defect charge states, these defects have much higher \( \Delta H \) and are not shown in Fig. 2a,b.) This means that once these defects form they will trap free electrons from the system and get negatively charged. Among these acceptor defects, the \( Al_{Ti}^- \) acceptors have the lowest \( \Delta H \) and thus they the most potent electron-trapping agents. For \( n_{LAO} < L_c \), the \( Al_{Ti}^- \) defects resulting from Ti \( \Leftrightarrow Al \) exchange trap all free electrons transferred from \( Ti_{Al}(S) \) defects, and hence no free carrier can occur. For \( n_{LAO} \geq L_c \), the \( \Delta H \) of \( [Ti_{Al}^- + Al_{Ti}^-] \) pair changes from negative to positive because of \( VO(S) \) (Fig. 4b), meaning that the concentration of \( Al_{Ti}^- \) defect resulting from Ti \( \Leftrightarrow Al \) exchange is reduced, compared with that formed below the \( L_c \). Therefore, the \( Al_{Ti}^- \) defect concentration is not sufficient to trap all 0.5e \( S_{2D}^{-1} \) electrons transferred from \( VO(S) \). Therefore, only a small fraction of 0.5e \( S_{2D}^{-1} \) can contribute to interface 2DEG.

The recently observed LaAlO₃ cation-stoichiometry effect on 2DEG formation⁴³ may also be understood within the above picture. For Al-rich LaAlO₃ film, where both A-site and B-site sublattices are fully occupied (hence having no cation vacancies), the \( Al_{Ti}^- \) antisites are the only electron-trapping defects and the incomplete trapping of 0.5e \( S_{2D}^{-1} \) interface charge by \( Al_{Ti}^- \) defects leads to interface conductivity. However, for La-rich LaAlO₃ film, where B-site sublattice is not fully occupied, the cation vacancies \( (V_{Ti} \) and \( V_{Al} \) also become the main electron-trapping agents, in addition to \( Al_{Ti}^- \). Although the concentration of \( Al_{Ti}^- \) is reduced, each cation vacancy induced in the La-rich film traps more electrons than an \( Al_{Ti}^- \). The insulating character can thus be then attributed to the complete interfacial electron trapping by both interfacial cation vacancies and \( Al_{Ti}^- \).

The picture of \( Al_{Ti}^- \) as the main electron-trapping agent may be extended to SrTiO₃/GdTiO₃ interfaces. The observed full carrier density of 0.5e \( S_{2D}^{-1} \) there⁶⁰ can be ascribed to the fact that both SrTiO₃ and GdTiO₃ have the same Ti atom at B-site sublattice and thus have no \( Al_{Ti}^- \)-like antisite defects at the interface.

Implication on how to increase the density of 2DEG: The above picture suggests that the main controlling factor for the interface carrier density is the concentration of the acceptor defects (mainly \( Al_{Ti}^- \) in stoichiometric or Al-rich film), which should be minimized for enhancing carrier density. Such \( Al_{Ti}^- \)-like electron-trapping defects may be completely removed by designing other oxide interfaces such as GdTiO₃/SrTiO₃ interfaces, whose bulk components have a common cation atom with multiple valence states.

The origin of the insulating nature of p-type interfaces. An intriguing fact is that the so-called p-type interfaces are not p-type (hole) conducting but are actually insulating. The defect-free polar-catastrophe model for p-type interface predicts a hole-conducting interface and an electron-conducting surface when \( n_{LAO} > \sim 7.3 \) uc (Supplementary Fig. 1) in contradiction with the insulating behaviour observed robustly in experiment. To explain this, defects must be involved. The emerging defect picture below differs from the literature model based solely on interfacial hole–polaron⁶¹ or interfacial hole-compensating \( VO \) defects⁵³,⁴⁴, which assumes that the interface has holes arising from the depopulation of the intrinsic SrTiO₃ valence bands.

Individual point defects alone at p-type interfaces can neither cause conductivity nor cancel the polar field. As was the case for n-type interfaces, Fig. 2b shows that the interface \( LaSr \) and \( TiAr \) are stable at their charge neutral states and have negligible or negative \( \Delta H \) at equilibrium \( E_F \). This means that they cause inevitable interfacial cation intermixing but induce no free carriers. The \( VO \) and other defects at the interface require too high \( \Delta H \) to form, and thus they do not produce free carriers either. For similar reason, each of the leading antisite defects \( [La_{Sr}, Sr_{La}, Ti_{Al}] \) and \( Al_{Ti}^- \) alone at p-type interfaces cannot cancel the polar field.

The spontaneously formed donor–acceptor defect pairs always cancel the polar field but do not induce free carriers. Among the four donor–acceptor defect pairs as indicted in Fig. 3b, the \( [La_{Sr} + Sr_{La}] \) (that is, pair 2) is energetically most favourable to cause polar field cancellation. For \( n_{LAO} \sim 4 \) uc, the \( [La_{Sr}(I) + Sr_{La}(S)] \) pairs have negative \( \Delta H \) (Fig. 4d) and can form spontaneously via La \( \Leftrightarrow Sr \) exchanges, whereas the \( [La_{Sr}(I) + V_{La}(S)] \) have too high \( \Delta H \) to form (Fig. 4c). Therefore, the polar field is cancelled by the charge transfer from \( La_{Sr}(I) \) to \( Sr_{La}(S) \), which can be expected from their relative defect levels (Fig. 3b) and their linear decreasing behaviour in \( \Delta H \) as a function of \( n_{LAO} \) (Fig. 4d). For \( n_{LAO} > 4 \) uc, the \( \Delta H \) of \( [La_{Sr}(I) + V_{La}(S)] \) become negative (Fig. 4c) and can also form spontaneously. Since \( V_{La} \) has a lower acceptor level than \( Sr_{La} \) (Fig. 3b), the polar field is cancelled by the charge transfer from \( La_{Sr}(I) \) to \( V_{La}(S) \), rather than to \( Sr_{La}(S) \). In absence of an electric field, Fig. 4d (open symbols) indicates that the La \( \Leftrightarrow Sr \) exchanges cannot occur anymore over a distance of \( \sim 4 \) uc. Unlike the case in n-type interfaces, the \( VO(S) \) defects in p-type interface always have too high \( \Delta H \) to form. The defects involved in polar field cancellation are all deep. The calculated equilibrium \( E_F \) according to those point defects turns out to be always around the middle of SrTiO₃ band gap. This means that both VBM and CBM are far away from the \( E_F \), and there are no free carrier arising from the depopulation of VBM and CBM in both interface and surface regions (whence insulating).

Implication on the design of 2D hole conductivity: Clearly, the formation of interfacial free holes is prevented by these
spontaneously formed deep La AO$_3$ defects that have donor level higher than the VBM at the interface. Therefore, to induce interfacial hole conductivity, one should search for the polar–nonpolar interfaces where all such donors have high enough formation energy to form or (ii) their donor levels below the VBM at the interface. Practically, the (ii) may be achieved more easily by searching for the polar material whose VBM is higher than the charge transition energy levels of those spontaneously formed interfacial donor defects.

**The origin of interface magnetism.** Distinct from previous models$^{35-34}$ that explain magnetism based on the intrinsic interfacial Ti$^{4+}$ ion in the SrTiO$_3$ (that is, not a defect), we find below that the local magnetic moment originates from the unionized deep Ti$_{Al}$ antisite defect (that is, Ti$^{3+}$-on-Al$^{5+}$ within LaAlO$_3$ side near the interface. The interface magnetism depends on the concentration and spatial distribution of such Ti$_{Al}$ defects. This picture explains not only why the magnetism appears at n-type interfaces with a similar critical thickness to that for 2DEG but also why the magnetism also appears at insulating p-type interfaces$^8$.

What causes local moment? As discussed earlier, for n-type interfaces, when $n_{LaO} < L_c$, the polar field in LaAlO$_3$ is cancelled by the charge transfer from Ti$_{Al}$(S) defects to the interface. These formed Ti$_{Al}$ defects are thus ionized, that is, Ti$_{Al}^{3+}$ (where superscript denotes the defect charge states). The Ti ion at this defect site has the oxidation states of $4+$, denoted as Ti$^{4+}$, which has no local magnetic moment. Moreover, noted before, when $n_{LaO} \geq L_c$, the polar field in LaAlO$_3$ is cancelled by the charge transfer to the interface from V$_{O}$(S) instead of Ti$_{Al}$. In absence of internal field, all Ti$_{Al}$(I) defects in the LaAlO$_3$ film are most stable in their charge neutral (or unionized) states, that is, Ti$_{Al}^{3+}$, where Ti appears as Ti$^{3+}$ oxidation state, having a finite local magnetic moment. Therefore, the interface magnetism at n-type interfaces because of those unionized Ti$_{Al}$ defects should also have a critical thickness of ~4 uc. For p-type interfaces, it is the charge transfer among the defects other than Ti$_{Al}$ defects that cancels the polar field in LaAlO$_3$. Thus, all Ti$_{Al}$ defects formed there are not ionized, having local magnetic moments, and cause interface magnetism.

The magnitude of local magnetic moment: The local moment of a single Ti$_{Al}$ defect at the interface can be estimated from that in bulk LaAlO$_3$, which is 0.84$\mu_B$ from our hybrid functional calculation. For ferromagnetic order as observed in the experiment, the total interface magnetic moment depends on the concentration of unionized Ti$_{Al}$ defects in LaAlO$_3$ and can be very small per Ti atom in average. The experimentally observed inhomogeneous landscape of magnetism that also varies from sample to sample$^{39}$ may be attributed to the various spatial distributions of Ti$_{Al}$ defects, which may be sensitive to sample preparation conditions (such as temperature and $P(O_2)$ and local strain.

The Ti$_{Al}$(I) defects within LaAlO$_3$ side being the origin of the local moment are more reasonable than V$_O$(I) in two aspects. First, the deep Ti$_{Al}$ defect is spatially localized and has an unambiguous local moment. In contrast, V$_O$ is a shallow donor that transfer electrons to the lower-energy interfacial Ti$^{2+}$ sub-bands that have light effective mass inside the interface plane$^{39}$, therefore, the resulting Ti$^{3+}$ may then be itinerant. Second, the Ti$_{Al}$ defects would form readily because of the small or negative $\Delta H$ of Ti$_{Al}$, whereas the interfacial V$_O$ requires significant energy to form and if formed it may be removed completely after annealing.

**Discussion**

We establish a physical link between polar discontinuity and defect formation: the polar discontinuity triggers spontaneous formation of certain defects that in turn cancel the polar field induced by polar discontinuity. It is the subtle interplay of those spontaneously formed surface vacancy defects and interfacial cation antisite defects that control the physics of the system by their formation energies and relative defect levels. Table 2 summarizes how those defects shown in Fig. 1 explain the leading experimental observations and puzzles in Table 1. The explanation leads to a set of design principles for both conductivity and magnetism at LaAlO$_3$/SrTiO$_3$ and other polar–nonpolar interfaces and enables the design of better polar–nonpolar interfaces.

Having ruled out the electronic reconstruction, interfacial V$_O$ and interfacial cation intermixing mechanism as the possible origin of 2DEG in our calculations, we conclude that the 2DEG at n-type interfaces with $n_{LaO} \geq L_c$ originates from the spontaneously formed V$_O$(S) defects. This conclusion stems from the finding that the donor level of deep V$_O$ in the LaAlO$_3$ side is higher than the SrTiO$_3$ conduction band edge at the interface. This finding explains why the formation energy of V$_O$(S) decreases linearly as $n_{LaO}$ increases. This linear decrease relation leads to some new controlling parameters for the critical thickness of sharp metal–insulator transition in absence of the electric field in the polar LaAlO$_3$ film. Instead of causing the 2DEG, the anti site defect pair turns out to play a key role in canceling the polar field, controlling the density of the 2DEG, and inducing the local magnetic moments at the interface (Table 2).

The emerging mechanism provides three distinctive predictions to be tested in experiment as further validation. (i) For

| Table 2 | The specific defects and their charge transfer processes that explain the leading experimental observations at stoichiometric LaAlO$_3$/SrTiO$_3$ interfaces. |
|---|---|---|---|
| **n-type interface structure** | **p-type interface structure** |
| $n_{LaO} < L_c$ | $n_{LaO} > L_c$ | $n_{LaO} < L_c$ | $n_{LaO} > L_c$ |
| **Polar field compensation** | Ti$_{Al}$(S) → Al$_{Ti}$(I) | V$_O$(S) → Al$_{Ti}$(I) and V$_2$(S) → CBM(I) | La$_{Sr}$(I) → Sr$_{La}$(S) |
| Origin of 2DEG/2DHG | No 2DEG: Al$_{Ti}$(I) traps all electrons from Ti$_{Al}$(S) | V$_2$(S) → CBM(I); Al$_{Ti}$(I) traps part of electrons from V$_O$(S) | No 2DHG: La$_{Sr}$(I) traps all holes from Sr$_{La}$(S) |
| Density of 2DEG/2DHG | Zero | < 0.5 e $S_{2DH}$ | Zero |
| Origin of critical thickness | Polar-field induced V$_O$(S) formation | Zero | Ti$^{3+}$-on-Al$^{5+}$ forms and induces local moment |
| Origin of interface magnetism | Ti$^{4+}$-on-Al$^{5+}$ forms and but has no local moment | Ti$^{3+}$-on-Al$^{5+}$ forms and induces local moment | Ti$^{3+}$-on-Al$^{5+}$ forms and induces local moment |

The "S" and "I" denote the LaAlO$_3$ free surface and LaAlO$_3$/SrTiO$_3$ interface, respectively. $S_{2DH}$ is the two-dimensional unit cell area.
n-type interfaces, the AlO$_2$-surface layer is dominated by Ti$_{Al}$ defects when $n_{TAl} < L_c$ and by V$_O$ defect when $n_{TAl} \geq L_c$. (ii) For p-type interfaces, the LaO$_2$-surface layer is dominated by Sr$_{La}$ and V$_{Al}$ defects, respectively, below and above an $L_c$ of ~4 uc. (iii) Ti$^{3+}$ and Ti$^{4+}$ signals exist in both sides of the interface. The appearance of the Ti$^{4+}$ signals should not be taken as a sign of conductivity. Whether the Ti$^{4+}$ signals detected by photoemission below the $L_c$ (refs 21,40,62,63) can be truly assigned to those Ti$^{4+}$ ions in the SrTiO$_3$ side should be revisited carefully. How these Ti$_{Al}$ local moments are ordered (ferromagnetic, or antiferromagnetic, or else) and whether and how they interact with the itinerant 2DEG are still open questions that should be investigated further.

**Methods**

**Computational techniques.** All calculations were performed using density functional theory and plane-wave projector-augmented wave method as implemented in the VASP code. An energy cutoff of 400 eV was used. The Brillouin zone was sampled by $8 \times 8 \times 1$ and $4 \times 4 \times 1$ k-point mesh for 1 $\times$ 1 and 2 $\times$ 2 in-plane supercell, respectively. The atomic forces were relaxed to be below 0.03 eV Å$^{-1}$. The in-plane lattice constant was fixed to 3.943 Å (the relaxed lattice constant of SrTiO$_3$, by GGA). In calculations, the 4-uc (~16 Å) vacuum layer was used and the dipole correction was always applied to remove artificial dipole interactions. The results in Figs 2 and 3 were obtained by using HSE hybrid functional on top of the GGA-relaxed structures.

**First principles defect theory.** The formation energy of a defect (D) calculated from $AH_D(E_F, \mu) = E_0 - \sum n_i (\mu_i + \Delta\mu_i) = \Delta E_n(E_F)$, where $E_0$ and $E_n$ are the total energies of a supercell with and without defect, respectively, and D is in charge state $n$. $n_i$ is the number of atoms of species $x$ needed to create a defect. $\Delta\mu_i$ is the Fermi energy relative to VRM ($E_F$). $\Delta\mu_i$ is the relative chemical potential of species $x$ with respect to its elemental solid (gas); $\rho_i^c$. The equilibrium Fermi energy was calculated self-consistently according to charge neutrality condition$^{69}$. The chemical potentials relative to their elemental solid (or gas) phase are taken as $\mu_i^c$. The energy was calculated self-consistently according to charge neutrality condition$^{69}$. 

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L.Y. carried out the calculations, analysed the results and wrote the paper. A.Z. initiated the study of this topic and contributed to the analysis of the results and to the writing of the paper.

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