Oxygen transport in single-crystal LaAlO₃ substrates

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The rates of oxygen incorporation into, and oxygen diffusion in, cubic, nominally undoped LaAlO₃ were investigated by means of isotope exchange experiments and subsequent time-of-flight secondary ion mass spectrometry analysis. ¹⁸O diffusion profiles were introduced into single-crystal samples by annealing in isotope-enriched molecular oxygen (¹⁸O₂) at various temperatures in the range 873 K $\leq T \leq 1173$ K at an oxygen activity of $aO_2 = 0.2$ or at various oxygen activities $2 \times 10^{-3} \leq aO_2 \leq 1$ at T = 983 K. All measured isotope profiles consisted of a sharp drop at the surface, attributed to hindered diffusion through a depletion space-charge zone, followed by a shallow decrease, attributed to faster diffusion equation yielded the tracer diffusion coefficient D^* , the surface exchange coefficient k^* , and the surface space-charge potential Φ_0 . The relatively high activation enthalpy of oxygen diffusion of $\Delta H_{D^*} = (0.90 \pm 0.06)$ eV was attributed to oxygen vacancies interacting with cation vacancies. The activation enthalpy for oxygen surface exchange was surprisingly low ($\Delta H_{k^*} < 3$ eV) in view of the large band gap of LaAlO₃ (≈ 5.6 eV).

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I. INTRODUCTION

 $A^{\text{III}}B^{\text{III}}O_3$ perovskites adopt a distorted perovskite structure (generally, orthorhombic or rhombohedral) at room temperature, exhibiting the ideal cubic structure only at elevated temperatures [1,2]. In the case of LaAlO₃ (lanthanum aluminate), the room-temperature structure displays rhombohedral ($R\bar{3}c$) symmetry, and the transition to the cubic ($Pm\bar{3}m$) form takes place at a temperature of $T = (815 \pm 10)$ K [3–5].

This unusually low transition temperature provides an optimal window of temperatures for studying oxide-ion diffusion in a *cubic* $A^{III}B^{III}O_3$ perovskite, i.e., without the distorted crystal structure and without the presence of domain walls complicating matters. Specifically, the temperatures are high enough for measurable diffusion profiles to be obtained in reasonable annealing times, but not so high that excessively long profiles result or complex equipment is required.

The transport of oxide ions in LaAlO₃-based systems has attracted attention for different reasons over the years [5–20]. Initially, the aim was to develop outstanding oxide-ion conducting electrolytes, and this entails replacing 10–20% of one or both of the native cations with lower-valent species in order to achieve high concentrations of oxygen vacancies. Later came the additional aim of understanding the fundamentals of anion migration by a vacancy mechanism in perovskites, but most experimental data referred to typical electrolyte compositions, and understanding anion-vacancy behavior in such concentrated solid solutions is far from trivial.

More recently, there is interest in oxygen diffusion in undoped, single-crystal LaAlO₃. Studies of thin-film oxide

In order to avoid such issues, in this study we subjected single-crystal samples of nominally undoped LaAlO₃ to isotope exchange anneals and determined the isotope diffusion profiles by means of time-of-flight secondary ion mass spectrometry (ToF-SIMS). Not only do such experiments probe solely the transport of oxygen, but they also provide direct information on the behavior of the defects responsible for diffusion, in this case, oxygen vacancies. In addition, they yield, for isotope introduction from the gas phase, the surface exchange coefficient, a coefficient that describes the dynamic equilibrium between oxygen molecules in the gas phase and oxygen ions in the solid [24]. Lastly, such experiments can reveal inhomogeneous distributions of oxygen defects and the presence of fast-diffusion paths [25]. In this regard, it is noted that various acceptor-doped perovskite systems [SrTiO₃, BaTiO₃, Pb(Zr, Ti)O₃] have all been shown to display a surface space-charge zone [26–33], in which oxygen vacancies are strongly depleted. A spacecharge layer depleted of oxygen vacancies is thus expected at the surface of LaAlO₃, and this needs to be confirmed or discounted.

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deposition onto perovskite substrates [21-23] have shown that oxygen diffuses from the substrate to the growing film during deposition at elevated temperatures. Quantitative studies of oxide-ion transport in nominally undoped or weakly acceptor-doped LaAlO₃ do exist [5,8,10,14,16,19,20], but there are evidently unidentified problems. The reported activation enthalpies for oxygen-vacancy migration scatter, namely, between 0.65 and 1.9 eV. Such scatter may be due to the use in some cases of polycrystalline samples rather than single crystals; in other cases, to incomplete characterization or knowledge of the samples under study; and in other cases, to the neglect of electronic contributions to the measured conductivity.

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II. THEORY

A. Bulk defect chemistry

The main assumption is that the nominally undoped singlecrystal samples of LaAlO₃ are in fact acceptor doped, with the acceptor dopants being compensated by oxygen vacancies:

$$[Acc']_{eff} = 2[v_0^{\bullet\bullet}], \tag{1}$$

where the defects are described with Kröger-Vink notation [34] and square brackets denote concentrations. This assumption is based on typical impurities (e.g., Ca^{2+} , Mg^{2+} , and Na^+) having a lower charge than the host cations and on the La:Al ratio probably deviating from exactly unity, with the imbalance generating cation vacancies. In other words, the effective concentration of acceptors contains the concentrations of divalent and univalent impurity cations and of cation vacancies:

$$[Acc']_{eff} = [Acc'] + 2[Acc''] + 3[v''_{Ia}] + 3[v'''_{AI}].$$
(2)

The assumption expressed on the right-hand side of Eq. (1)—that oxygen vacancies form to charge compensate acceptor-type species—is based on the evident ease (relative to other modes of charge compensation) with which oxygen vacancies form in LaAlO₃. Doping (or indeed, substitution) with acceptor-type cations leads to LaAlO₃ becoming an oxide-ion conducting electrolyte.

Here, it is important to note that Eq. (1) is consistent not only with isothermal conductivity data obtained as a function of oxygen activity [8,10,19] but also, as we will later show, with our tracer diffusion data.

B. Space-charge thermodynamics

Space-charge zones will form at an extended defect (surface, grain boundary, or dislocation) in a locally electroneutral system, if the system can lower its Gibbs energy by redistributing charge carriers from the bulk phase to the extended defect (or vice versa). The extended defect thus acquires a charge, which is compensated by an enveloping diffuse spacecharge zone [35,36]. The driving energy for redistribution, and thus for space-charge formation, is the Gibbs energy of segregation of the charge carrier *j*, that is, the difference in the Gibbs formation energy of *j* between the core of the extended defect (^c) and the bulk (^b): $\Delta_{seg}g_j = \Delta_f g_j^c - \Delta_f g_j^b \neq$ 0. The equilibrium situation corresponds to the electrochemical potential of a mobile charge carrier, $\tilde{\mu}_j$, being constant throughout the system. For a dilute solution of noninteracting defects, $\tilde{\mu}_j$ can be assumed [37] to take the form

$$\tilde{\mu}_j = \Delta_{\rm f} g_j + k_{\rm B} T \ln\left(\frac{[j]}{N_j - [j]}\right) + z_j e \phi, \qquad (3)$$

where N_j is the volume density of sites available for j, z_j is the charge number of j, and ϕ is the electric potential.

For the specific case of an LaAlO₃ surface, we make some assumptions. First we assume that of the two point defects considered in this paper [cf. Eq. (1)] only oxygen vacancies are mobile at the temperatures of interest [38,39], and hence, that $\Delta_{seg}g_v$ is the only relevant driving energy for defect redistribution. (Nonzero values of $\Delta_{seg}g_a$ play no role, since the acceptor defects are immobile and cannot redistribute.) We also assume that $\Delta_{seg}g_v$ exhibits a steplike profile (the abrupt core|space-charge model [40]), displaying a negative value in the surface core and zero everywhere else [35,41].

Within the space-charge layer, the concentration of oxygen vacancies depends on the electric potential. The variation in electric potential is obtained by solving for the domain of the solid the Poisson–Boltzmann equation,

$$\epsilon_0 \epsilon_r \frac{d^2 \phi}{dx^2} = -e[\operatorname{Acc'}]_{\text{eff}} \left[1 - \exp\left(\frac{-2e\phi(x)}{k_{\text{B}}T}\right) \right], \quad (4)$$

with the boundary conditions $\nabla \phi(\infty) = 0$ and $\Phi_0 = \phi(0) - \phi(\infty)$ (Φ_0 is the space-charge potential); and with relative dielectric permittivity $\epsilon_r = 25$ [5] and [Acc']_{eff} = 1.7 × 10²⁴ m⁻³ (see Sec. IV A).

C. Tracer diffusion through space-charge layers

The experiment revealing the surface space-charge layer relies on the fact [28] that the tracer diffusion coefficient of oxygen depends on the concentration of oxygen vacancies:

$$D^* = f^* D_{\mathbf{v}} \frac{[\mathbf{v}_0^{\bullet\bullet}]}{[\mathbf{O}_0^{\times}]},\tag{5}$$

where f^* is the tracer correlation factor, D_v is the diffusivity of oxygen vacancies, and $[O_O^\times]$ is the concentration of oxygen ions on regular oxygen sites. Thus, if $[v_O^{\bullet\bullet}]$ becomes a function of spatial coordinate, then D^* will show the same spatial variation,

$$D^{*}(x) = f^{*}D_{v}\frac{[\mathbf{v}_{0}^{\bullet\bullet}](x)}{[\mathbf{O}_{0}^{\times}](x)} = D^{*}\exp\left(\frac{-2e\phi(x)}{k_{\mathrm{B}}T}\right).$$
 (6)

The isotope profile is then obtained by solving the diffusion equation,

$$\frac{\partial n^*}{\partial t} = \frac{\partial}{\partial x} \left(D^*(x) \frac{\partial n^*}{\partial x} \right),\tag{7}$$

for the isotope fraction n^* , subject to the initial and boundary conditions

$$n^*(x \ge 0, t = 0) = n^*_{\text{bg}},$$
 (8a)

$$n^*(x = \infty, t > 0) = n_{bg}^*,$$
 (8b)

$$k^*[n_g^* - n^*(x=0,t)] = -D^*(x=0) \frac{\partial n^*}{\partial x}\Big|_{x=0}.$$
 (8c)

That is, the medium at t = 0 has a uniform background isotope fraction n_{bg}^* ; the medium is semi-infinite for the chosen diffusion time t; and isotope exchange at the surface occurs from a large volume of gas of isotope fraction n_g^* with surface-limited kinetics. k^* is the surface exchange coefficient.

III. EXPERIMENT

Nominally undoped single crystals of LaAlO₃ were obtained commercially (CrysTec GmbH, Berlin, Germany). They measured 10 mm \times 5 mm \times 1 mm and had one large face polished. All crystals had been cut from the same wafer to minimize differences in the type and amount of impurity species between the samples. ToF-SIMS analysis of the as-received crystals indicated the presence of Ba and Ca as impurities. Regardless of whether these species reside on the *A* site or the *B* site of the perovskite lattice, their lower charge (of 2+) relative to those of the host cations means that they act as acceptors. Given the possibility of small imbalances in the La:Al ratio, we consider the impurity level as a lower limit.

Isotope exchange experiments

To perform an oxygen isotope exchange experiment, it is necessary that the oxide sample is first in chemical equilibrium with the surrounding oxygen gas. To achieve this, an as-received crystal was held for a time t_{eq} ($t_{eq} > 10t$, with t being the exchange time) at the temperature and oxygen activity of interest in molecular oxygen of natural isotope abundance. Subsequently, the sample was quenched to room temperature to freeze in the equilibrium composition, and the gaseous oxygen was removed. In the exchange step, the sample was exposed to ¹⁸O-enriched gas for an anneal time t at the same temperature and oxygen activity as previously used, after which the sample was quenched to room temperature to freeze in the isotope profile. The actual ¹⁸O isotope fractions of the equilibrating gas and the isotope-enriched gas were determined by oxidizing pieces of single-crystal silicon and analyzing the isotope fractions by ToF-SIMS. Further information about this standard procedure can be found elsewhere [42,43].

The oxygen isotope profiles in the single crystals were obtained by time-of-flight secondary ion mass spectrometry on a TOF-SIMS IV machine (IONTOF GmbH, Münster, Germany). A high-energy Ga⁺ gun was used to generate secondary ions for analysis, a low-energy Cs⁺ gun was used for sputter etching of the sample, and a low-energy electron gun was used for charge compensation. The Ga⁺ gun was operated in burst mode [26] at an energy of 25 keV and a cycle time of 45 μ s. The depth profiles (up to 15 μ m) were obtained with 2-keV Cs⁺ ions and a sputter current around 140 nA. A sputter raster of 250 μ m × 250 μ m was used, together with an analysis raster of 70 μ m \times 70 μ m to avoid crater-wall effects. The pressure in the main chamber of the SIMS machine was lower than 10^{-9} mbar during the measurement. The detection of negative ions allows the calculation of the isotope fraction $n^{*} \{= [{}^{18}O]/([{}^{18}O] + [{}^{16}O])\}$ either from the atomic O⁻ or from the molecular O_2^- species. Both methods yielded similar results, as expected, with the former method providing better signal-to-noise levels. Detailed information for calculation of the isotope fraction can be found elsewhere [26,28].

Crater depths were determined after the SIMS analysis with an NT1100 interference microscope (Veeco Instruments, Oyster Bay, NY).

The single crystals developed, of course, domains as they were cooled from the annealing conditions through the phase-transition temperature. The domains that formed were sufficiently large that each ToF-SIMS measurement took place within a single domain. This is not important for the determination of the isotope fraction, since it is unaffected by domain formation, but it does allow the crater depth to be determined more precisely, since the surface around the crater refers to a single domain.

IV. RESULTS

A. Isotope profiles

Each measured isotope profile showed the same form with two features (see Fig. 1): a sharp drop in normalized isotope fraction over the first few nanometers, followed by a shallow decrease over some micrometers. The shapes of the



FIG. 1. Isotope profile obtained for a single crystal of LaAlO₃ after an isotope anneal at T = 1023 K and $aO_2 = 0.2$ for t = 15 min. Experimental data are shown as black symbols; the numerical description (single solution of the diffusion equation) is shown as a red line: (a) double linear plot, with the inset showing the first 30 nm; (b) double logarithmic plot.

two features strongly suggest that the first corresponds to hindered diffusion through a depletion space-charge layer near the surface; and that the second, longer feature corresponds to diffusion in a homogeneous medium. Indeed, a numerical solution of the diffusion equation, Eq. (7), based on the spatial variation of tracer diffusion coefficient given by the solution to Eq. (4), is able to describe an entire profile, as shown in Fig. 1. Such a description yielded the tracer diffusion coefficient D^* , the oxygen surface exchange coefficient k^* , and the surface space-charge potential Φ_0 . A good description of the first feature of all measured isotope profiles was found to be possible with $[Acc']_{eff} = 1.7 \times 10^{24} \text{ m}^{-3}$. Values of D^* , k^* , and Φ_0 obtained as a function of temperature *T* or oxygen activity aO_2 are summarized in Figs. 2, 3, and 4, respectively.

It is worth emphasizing how rapidly oxygen diffusion occurs in this system. Even though oxygen diffusion is strongly impeded by the depletion space-charge zone, after only 15 min the isotope diffusion front has penetrated several micrometers into this LaAlO₃ sample at T = 1023 K.

B. Tracer diffusion

Tracer diffusion coefficients D^* obtained as a function of oxygen activity aO_2 and of temperature T are plotted in



FIG. 2. Oxygen tracer diffusion coefficients obtained for cubic LaAlO₃ (a) as a function of oxygen activity at T = 983 K and (b) as a function of inverse temperature at $aO_2 = 0.2$.

Figs. 2(a) and 2(b), respectively. Describing the former with a power law,

$$D^* \propto (a\mathcal{O}_2)^{m_{D^*}},\tag{9}$$

we obtain $m_{D^*} = -(0.024 \pm 0.025)$, where the error given is the standard error in fitting a power law to the data. From Eq. (5), we recognize that

$$m_{D^*} = \left(\frac{\partial \ln D^*}{\partial \ln a O_2}\right)_T = \left(\frac{\partial \ln [\mathbf{v}_0^{\bullet\bullet}]}{\partial \ln a O_2}\right)_T,\tag{10}$$

since neither D_v nor f^* varies with oxygen activity; and the variation in $[O_O^{\times}]$ is negligible. m_{D^*} being zero within experimental error thus indicates that $[v_O^{\bullet\bullet}]$ does not vary with aO_2 . These data are, therefore, consistent with Eq. (1), which states that the concentration of oxygen vacancies is fixed by the concentration of acceptor-type dopants. One consequence of this behavior is that oxygen vacancies are present in nominally undoped LaAlO₃ substrates, even after high-temperature annealing in pure oxygen $(aO_2 = 1)$.

The second consequence concerns the interpretation of the data in Fig. 2(b). This Arrhenius plot yields an activation enthalpy of oxygen tracer diffusion of $\Delta H_{D^*} = (0.90 \pm 0.06)$ eV. In general, ΔH_{D^*} is the sum of two terms, the activation enthalpy of oxygen-vacancy migration and the enthalpy



FIG. 3. Oxygen surface exchange coefficients obtained for cubic LaAlO₃ (a) as a function of oxygen activity at T = 983 K and (b) as a function of inverse temperature at $aO_2 = 0.2$.

of oxygen-vacancy generation:

$$\Delta H_{D^*} = -k_{\rm B} \left(\frac{\partial \ln D^*}{\partial (1/T)} \right)_{a O_2}$$

= $-k_{\rm B} \left(\frac{\partial \ln D_{\rm v}}{\partial (1/T)} \right)_{a O_2} - k_{\rm B} \left(\frac{\partial \ln \left[v_{\rm O}^{\bullet \bullet} \right]}{\partial (1/T)} \right)_{a O_2}$
= $\Delta H_{\rm mig,v} + \Delta H_{\rm gen,v},$ (11)

if f^* and $[O_O^{\times}]$ are assumed to be temperature independent. Given that $[v_O^{\bullet\bullet}]$ is fixed by $[Acc']_{eff}$, as indicated in Eq. (1), $\Delta H_{\text{gen},v} = 0$, and thus the interpretation is simplified: $\Delta H_{\text{mig},v} = \Delta H_{D^*} = (0.90 \pm 0.06) \text{ eV}.$

C. Surface exchange

The behavior of the surface exchange coefficient k^* as a function of aO_2 and T is shown in Figs. 3(a) and 3(b), respectively. A power-law description of the former set of data yields a power-law exponent $m_{k^*} = (0.431 \pm 0.134)$. Because of the large error, we do not consider these data further. We note that the value expected for a wide-band-gap, acceptor-doped oxide is $m_{k^*} = 0.25$ [24,44].

As a function of temperature [Fig. 3(b)], k^* can be described not only with a single activation enthalpy of $\Delta H_{k^*} = (2.31 \pm 0.13)$ eV but also with two activation enthalpies, one of $\Delta H_{k^*} = (2.62 \pm 0.34)$ eV for a high-temperature regime



FIG. 4. Surface space-charge potentials obtained for cubic LaAlO₃ (a) as a function of oxygen activity at T = 983 K and (b) as a function of temperature at $aO_2 = 0.2$. The lines indicate the predictions of the thermodynamic model with $\Delta_{\text{seg}}g_v = -(1.25 \pm 0.05)$ eV.

and one of $\Delta H_{k^*} = (1.85 \pm 0.22) \text{ eV}$ for a low-temperature regime. Many acceptor-doped oxides show a change in activation enthalpy in this range of temperatures [44].

D. Space-charge potential

The space-charge potential is seen in Fig. 4 to depend weakly on temperature and to be independent of oxygen activity. By combining Eq. (3), a solution to Eq. (4), and the condition that the charge at the surface from vacancy segregation is compensated by the charge of the space-charge layer $(Q^c + Q^{scl} = 0)$, one can obtain $\Phi_0(T, aO_2)$ for given $\Delta_{seg}g_v$ and $[Acc']_{eff}$. We found that $\Delta_{seg}g_v = -(1.25 \pm 0.05) \text{ eV}$ is able to describe the behavior of Φ_0 both as a function of Tand as a function of aO_2 .

The fact that Φ_0 varies slightly with *T* but not with aO_2 is also consistent [35] with the bulk electroneutrality condition of Eq. (1).

V. DISCUSSION

A. Diffusion and conductivity

Since all ion transport data reported for nominally undoped or weakly acceptor-doped LaAlO₃ refer to the electrical conductivity [5,8,10,14,16,19,20], we converted our tracer





FIG. 5. Ionic conductivities reported for LaAlO₃ materials: A, this study (from D^*); B, Kilner *et al.* [8]; C, Mizusaki *et al.* [10]; D, Nguyen *et al.* [14], E, Chen and Fung [16]; F, Hayward *et al.* [5]; G, Gunkel *et al.* [19]; and H, Verma *et al.* [20].

diffusion coefficients into ionic conductivities with the aid of the Haven ratio,

$$H_{\rm r} = \frac{D^*}{D^{\sigma}},\tag{12}$$

which links the tracer diffusion coefficient to the conductivity diffusion coefficient D^{σ} ; and with the aid of the Nernst-Einstein equation,

$$\sigma = \frac{D^{\sigma}[O_{O}^{\times}](2e)^{2}}{k_{\rm B}T},\tag{13}$$

which links D^{σ} to the conductivity σ . In general, the Haven ratio can be expressed [45,46] as the quotient of the tracer and conductivity correlation coefficients, $H_{\rm r} = f^*/f^{\sigma}$. We recently determined [47] that $f^{\sigma} = 6/Z$ (where Z is the number of jump neighbors and equal to 8 for a cubic perovskite). The conductivity calculated in this way is compared with literature data in Fig. 5.

At first sight, one finds that data sets G and H [19,20] agree most closely with data set A, both in terms of the absolute magnitude and activation enthalpy. Differences are expected with regard to data sets B, C, and D. The very low values of data set B are consistent with the presence of a (highly resistive) second phase at the grain boundaries, as noted by the authors [8]. The higher values of data sets C and D are consistent with these samples containing more oxygen vacancies as they were purposely doped with acceptor cations (C, 0.8% Ca_{La}; D, 1.0% Sr_{La}) [10,14]. Data sets E and F [5,16] are problematic. From their absolute values (i.e., comparable to data sets C and D), one would conclude, if the conductivity is ionic, that the samples were characterized by large amounts of acceptor impurities or substantial cation nonstoichiometry, but from the measurement conditions (i.e., in air), one would conclude that the conductivities are not ionic, but electronic in origin. The situation is not that clear, however, since data set H was also measured in air [20]. It is also surprising that data set H shows no change in activation energy at the phasetransition temperature, and that data set F shows a change but not at the phase-transition temperature (the hole conductivity, it is noted, may also show a change in activation enthalpy, as reported by Mizusaki *et al.* [10]). Considering all data, therefore, we conclude that, if we want data that refer without doubt to ionic transport in the bulk phase of undoped LaAlO₃, we are left with data sets A (from tracer diffusion) and G [conductivity extracted from $\sigma(T, aO_2)$]. All other data sets can be discounted because the reported conductivity may be electronic, may refer to the grain boundaries, or does refer to purposely doped material (or some combination thereof).

B. Activation enthalpy of vacancy migration

Having identified reliable data for oxide-ion transport (data sets A and G), we now turn to the issue of the activation enthalpy. These two studies yield values of $(0.90 \pm 0.06) \text{ eV}$ and $(1.14 \pm 0.01) \text{ eV}$. Simulations predict, in comparison, far lower barriers for oxide-ion migration by a vacancy mechanism. From density-functional-theory (DFT) calculations [48–50], values of 0.63, 0.54, and 0.64 eV were obtained, and these are in very good agreement with those from classical pair potential simulations (0.57 and 0.7 eV) [9,51].

We attribute the higher activation enthalpies observed experimentally to interactions between oxygen vacancies and acceptor-type species [52–55]. Given that the samples in both cases (data sets A and G) were nominally undoped, identifying the nature of the acceptor-type species is not trivial. We contend that alkaline-earth impurities are unlikely to be responsible, on the basis of data set C, obtained by Mizusaki et al. [10] for Ca-doped, single-crystal LaAlO₃. Their value of (0.75 ± 0.02) eV is higher than the predicted activation enthalpies [9,48–51], but not high enough. This leaves [see Eq. (2)] either alkali impurities (e.g., $Na'_{1,a}$) or cation vacancies (i.e., $v_{La}^{\prime\prime\prime}$ or $v_{A1}^{\prime\prime\prime}$) as the dominant acceptor-type species. The latter defects, in particular, are expected to produce much stronger effects [55], and activation barriers calculated for oxygen-vacancy migration next to a neighboring lanthanum or aluminium vacancy are rather high, at 1.13 and 1.35 eV [48]. The effective activation enthalpy obtained in transport studies refers to long-range transport, and since cation vacancies are far less mobile than anion vacancies in perovskite oxide, the oxygen vacancies have to leave a cation vacancy to migrate through the crystal. That is, the effect of an oxygen vacancy leaving a cation vacancy (i.e., the trapping energy) also needs to be taken into account to explain quantitatively the experimental values of $\approx 1 \text{ eV}$. We cannot rule out that alkali impurities play a role, but we have no evidence to suggest that they are present in sufficient amounts. Thus our oxygen diffusion results strongly suggest that nominally undoped LaAlO₃ single crystals contain cation vacancies.

In order to confirm that cation vacancies are present in these LaAlO₃ substrates and responsible for the high activation enthalpies, one would have to employ positron annihilation spectroscopy (PAS) and molecular dynamics (MD) simulations. PAS would confirm the presence of cation vacancies (see, e.g., Ref. [56] for SrTiO₃). A series of MD simulations with different acceptor-type defects that directly yield oxygen tracer diffusion coefficients as a function of temperature (see, e.g., Ref. [55] for LaMnO₃) would allow the most likely culprits to be identified (and others to be excluded).



FIG. 6. Diffusivity of oxygen vacancies in nominally undoped LaAlO₃ substrates: A, this study (from D^*); G, Gunkel *et al.* [19] (from σ).

C. Diffusivity of oxygen vacancies

In Fig. 6 we compare oxygen-vacancy diffusivities calculated from data sets A and G for nominally undoped LaAlO₃ with [Acc']_{eff} = 1.7×10^{24} m⁻³ (samples in both cases obtained from the same supplier). We find that the data sets differ by a factor of approximately 4, and we suggest one particular reason for this difference (assuming experimental error is negligible). In calculating D_v , we have treated the oxygen vacancies as noninteracting species (and used $f^* = 0.69$ and $f^{\sigma} = 6/8$). The results of the previous section indicated, however, that the oxygen vacancies interacted strongly with acceptor-type species (most probably $v_{La}^{''}$ or $v_{Al}^{''}$). Thus the correct calculation of D_v requires values of f^* and f^{σ} for oxygen vacancies interacting with cation vacancies, and these are not at present available.

Since the difference between the data sets is relatively small, we ignore it and fit all the data to obtain an expression for D_v in the temperature range 850 K $\leq T \leq 1188$ K,

$$\ln[D_{\rm v} \ ({\rm m}^2/{\rm s})] = -(10.3 \pm 2.4) - \frac{(1.09 \pm 0.21) \,{\rm eV}}{k_{\rm B}T}.$$
 (14)

This expression corresponds to the diffusivity of oxygen vacancies in nominally undoped, single-crystal LaAlO₃ (with probable cation nonstoichiometry).

This may seem rather specific, but it needs to be borne in mind that thin films of perovskites produced by pulsed laser deposition contain high concentrations of cation vacancies (well above equilibrium) on one or both sublattices [56–58]. To a first approximation, therefore, this expression is also applicable to oxygen-vacancy diffusion in thin-film LaAlO₃.

D. Oxygen surface exchange

Surface exchange describes the dynamic equilibrium between oxygen as molecules in the gas phase and oxygen as ions in the solid. The process has to involve a series of individual reaction steps (e.g., for the forward reaction: adsorption, dissociation, charge transfer, and incorporation into a vacancy) and may involve various possible reaction intermediates (e.g., $O_{2,ad}^{-}$, $O_{2,ad}^{-}$, and O_{ad}^{-}). The details of the reaction are a subject of intense debate [24,44,59–69].



FIG. 7. Comparison of surface exchange coefficients for selected perovskites: LaAlO₃ single crystals (this study), SrTiO₃ single crystals (De Souza *et al.* [30]), BaTiO₃ single crystals (Kessel *et al.* [31]), and La_{0.9}Sr_{0.1}Ga_{0.8}Sr_{0.2}O_{2.85} ceramics (Ishihara *et al.* [70]).

In Fig. 7 we compare the surface exchange coefficients obtained for single-crystal LaAlO₃ (we have assumed the two-regime analysis) with those reported for single-crystal SrTiO₃ [30], single-crystal BaTiO₃ [31], and ceramic La_{0.9}Sr_{0.1}Ga_{0.8}Sr_{0.2}O_{2.85} [70]. In this plot we have reinterpreted the data for BaTiO₃ and for La_{0.9}Sr_{0.1}Ga_{0.8}Sr_{0.2}O_{2.85}, dividing the data into a high-temperature and a low-temperature regime, rather than assuming the original analysis of a single activation enthalpy for the entire range. In both cases, the division into two regimes appears to give a superior description of the data. (This is one reason why we prefer the two-regime analysis for LaAlO₃.)

The reason for the change in activation enthalpy is believed to be a change in mechanism. At high temperatures, the rate-determining step, according to a variety of studies [44,60,65,67], is charge transfer, most likely of electrons from the conduction band of the oxide to the electronic level of the adsorbed oxygen species. At lower temperatures, the presence of small amounts of H₂O in the isotope-enriched annealing gases [44,71] (perhaps through adsorbed OH groups [72,73]) provides a faster path for oxygen incorporation. This also explains why the transition temperature may vary from study to study (as it depends on the particular apparatus in which the experiments were carried out).

The key features of the charge-transfer mechanism [44] are the detailed electronic band structure of the material (including defect-induced states), the position of the Fermi level within the band gap (as this determines the concentration of conduction-band electrons), and the position of the adsorbate level relative to the conduction-band edge. Such knowledge is not available at present, hindering a quantita-

tive analysis. We restrict ourselves, therefore, to qualitative comments. BaTiO₃, SrTiO₃, and La_{0.9}Sr_{0.1}Ga_{0.8}Sr_{0.2}O_{2.85} all have band gaps around 3 eV [74-77], whereas LaAlO3 has a band gap of 5.6 eV [78]. On this basis one would expect LaAlO₃ to exhibit the lowest rates of surface exchange; and one would expect La_{0.9}Sr_{0.1}Ga_{0.8}Sr_{0.2}O_{2.85} to exhibit rates lower than BaTiO₃ and SrTiO₃, on account of the high acceptor concentrations (10% Sr and 20% Mg) shifting the Fermi level downwards. What is observed, however, is that LaAlO₃ and La_{0.9}Sr_{0.1}Ga_{0.8}Sr_{0.2}O_{2.85} exhibit surprisingly high rates of oxygen surface exchange. If the mechanism for the hightemperature regime is indeed determined by electron transfer (and it is difficult to see why it would not be); and if there is a common cause for these two systems, we tentatively attribute the surprisingly high values of k^* to the presence of La (and thus to 5d electron states [79] or 4f states characteristic of the early rare earths, such as Ce). Detailed experimental studies of electronic band structures and surface exchange rates are required to examine this hypothesis.

VI. CONCLUDING REMARKS

We studied oxygen transport in single crystals of nominally undoped LaAlO₃ using isotope exchange experiments. From comparisons with literature data, we concluded that there are doubts as to whether certain published conductivity data refer to ion conduction in the bulk phase of undoped LaAlO₃. In addition, we concluded that in single-crystal substrates, cation vacancies are responsible for the high activation enthalpy of oxygen-vacancy migration (of ca. 1 eV). Given that perovskite thin films are generally characterized by high concentrations of cation vacancies, our data are thus applicable to oxygenvacancy diffusion in thin-film LaAlO₃.

The rate of oxygen surface exchange was found to be much faster than would be expected for such a wide-band-gap, acceptor-doped perovskite. We tentatively attributed the surprisingly behavior to the presence of La, and emphasized the need for detailed experimental information on the electronic band structure of LaAlO₃ and other La-containing perovskites in order to understand this behavior.

On a secondary note, we demonstrated some of the diverse benefits of performing oxygen isotope exchange experiments with SIMS analysis: monitoring solely oxide-ion migration, determining surface exchange coefficients, revealing inhomogeneous point-defect distributions and quantifying the surface space-charge potential.

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