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# Unraveling the formation of oxygen vacancies on the surface of transition metal-doped ceria utilizing artificial intelligence†

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Ceria has been extensively utilized in different fields, with surface oxygen vacancies playing a central role. However, versatile oxygen vacancy regulation is still in its infancy. In this work, we propose an effective strategy to manipulate the oxygen vacancy formation energy *via* transition metal doping by combining first-principles calculations and analytical learning. We elucidate the underlying mechanism driving the formation of oxygen vacancies using combined symbolic regression and data analytics techniques. The results show that the Fermi level of the system and the electronegativity of the dopants are the paramount parameters (features) influencing the formation of oxygen vacancies. These insights not only enhance our understanding of the oxygen vacancy formation mechanism in ceria-based materials to improve their functionality but also potentially lay the groundwork for future strategies in the rational design of other transition metal oxide-based catalysts.

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## 1. Introduction

Ceria-based materials are the key components in catalysts used for automotive exhaust treatment and hydrogen purification, as well as in many other functional materials, such as oxide-ion conductors and sensors.<sup>1–5</sup> In all such applications, the formation of oxygen vacancies ( $O_v$ s) is a critical step. These  $O_v$ s serve as anchor sites to stabilize small transition metal (TM) clusters and prevent them from aggregating in ceria-supported TM catalysts.<sup>6–8</sup> Two electrons remaining after the removal of one neutral oxygen localize in the empty 4f orbital of Ce,<sup>9,10</sup> resulting in the reduction of two Ce cations from the +4 oxidation state to the +3 oxidation state; this reduction changes the surface chemistry of the ceria and consequently its cata-

lytic performance.<sup>11,12</sup> Thus, the effective regulation of the  $O_v$  formation energy is extremely important, especially in catalytic applications.

In recent decades, tremendous efforts have been devoted to designing and synthesizing TM oxides with optimized  $O_v$  populations and distributions. Some examples of such efforts include modifying the  $O_v$  dynamic behavior and concentration of  $CeO_2$  by suitable doping and strong metal–support interactions,<sup>13–18</sup> tuning the oxygen storage capacity and  $O_v$  formation energy of  $CeO_2$  through a large biaxial strain,<sup>19</sup> and altering the formation, distribution, and mobility of  $O_v$ s and ion defects of  $CeO_2$  *via* dislocation.<sup>20</sup> TM doping has been thoroughly utilized to manipulate the surface chemistry and  $O_v$  behavior of ceria-based catalysts.<sup>21–23</sup> Ke and coworkers proposed a robust approach for tuning the CO oxidation activity over  $CeO_2$  nanowires through careful modulation of the local structure and surface states by doping lanthanides with continuous variation in the ionic radii.<sup>21</sup> Zhang *et al.* successfully synthesized  $CeO_2$  solid solutions with an ultrahigh manganese doping concentration and found that highly reducible  $Mn^{4+}$  ions strongly facilitate the migration of  $O_v$ s from the bulk to the surface.<sup>22</sup> Jiang and coworkers found that cobalt-doped ceria nanosheets possess high efficiency toward the hydrogen evolution reaction due to the increased concentration of  $O_v$ s and the increased number of active sites.<sup>23</sup>

Theoretical calculations also play an essential role in investigating the origins of the increased performance of TM-doped ceria materials.<sup>24–28</sup> Guo *et al.* investigated the effects of Pd,

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Ru, and Cu dopants on the reduction selectivity of CO<sub>2</sub> on CeO<sub>2</sub>(111) and found that the doped metals distorted the local geometry of the ceria surface by weakening the Ce–O bond and thus generating highly active O<sub>v</sub> sites.<sup>24</sup> Yang *et al.* investigated the CO oxidation reaction on Cu-adsorbed and Cu-doped ceria systems and found that the Cu-adsorbed system inhibited the formation of O<sub>v</sub>s, while the Cu-doped system facilitated the formation of O<sub>v</sub>s.<sup>26</sup> Krcha and coworkers systematically calculated the O<sub>v</sub> formation energies and reaction activity for hydrocarbon conversion on various TM-doped CeO<sub>2</sub>(111) surfaces, and clear periodic trends in the O<sub>v</sub> formation energies and C–H bond activations were observed.<sup>25</sup> Despite extensive efforts, the mechanisms underlying the changes in the dopant-induced O<sub>v</sub> formation energy remain unclear.

In this work, we performed systematic calculations on the stabilities and surface O<sub>v</sub> formation energies for 97 TM-doped ceria systems, with dopants occupying the surface cerium sites. An in-depth analysis was conducted to explore the correlations between the properties of these systems (including stabilities and surface O<sub>v</sub> formation energies) and the features of the dopants, employing a combined approach of sure independence screening and sparsifying operator (SISSO)<sup>29</sup> and subgroup discovery (SGD) methodologies.<sup>30–35</sup> These techniques facilitated the unveiling of the underlying mechanisms that drive the observed trends in the data.

## 2. Methods

Spin-polarized DFT calculations were carried out using the generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof (PBE) as implemented in the Vienna *ab initio* Simulation Package (VASP).<sup>36,37</sup> A Hubbard-type term  $U = 5.0$  eV was used for the Ce 4f states to describe the localization of the excess charges, which is within the range of suitable values

to describe reduced ceria-based systems.<sup>38</sup> The Kohn–Sham valence states were expanded in a plane-wave basis set with a cutoff energy of 400 eV. The core–valence interactions were represented using the projector augmented wave (PAW) approach,<sup>39</sup> where the (4f, 5s, 5p, 5d, 6s) and (2s, 2p) states of the Ce and O atoms were treated as valence states. A periodic slab with a (4 × 4), (3 × 4), and (4 × 4) surface unit cell was employed to model the CeO<sub>2</sub>(100), CeO<sub>2</sub>(110), and CeO<sub>2</sub>(111) surfaces, respectively. The slabs consisted of nine, five, and twelve atomic layers, respectively, with an additional vacuum layer of 15 Å. During the geometry optimization, the bottom two layers (O–Ce), three layers (O–Ce–O), and three layers (O–Ce–O) were held fixed at their bulk positions for CeO<sub>2</sub>(100), CeO<sub>2</sub>(110), and CeO<sub>2</sub>(111) surfaces, respectively. Due to the large supercell dimensions, the *k*-point sampling was restricted to the  $\Gamma$  point. Structures were fully relaxed until the maximum force on each atom becomes less than 0.05 eV/Å. The surface energies for CeO<sub>2</sub>(100), CeO<sub>2</sub>(110), and CeO<sub>2</sub>(111) are collected in Table S1† and benchmarked against the existing literature values.

The formation energy ( $\Delta E_F$ ) of the TM-doped CeO<sub>2</sub> surfaces was calculated using formula (1):

$$\Delta E_F = E_{\text{TM-slab}} - E_{\text{slab}} + \frac{E_{\text{bulk}}^{\text{Ce}}}{N_{\text{bulk}}^{\text{Ce}}} - \frac{E_{\text{bulk}}^{\text{TM}}}{N_{\text{bulk}}^{\text{TM}}} \quad (1)$$

where  $E_{\text{TM-slab}}$  is the total energy of the whole system,  $E_{\text{slab}}$  is the energy of the clean CeO<sub>2</sub> surfaces,  $E_{\text{bulk}}^{\text{Ce}}$  is the energy of the conventional cell of ceria,  $N_{\text{bulk}}^{\text{Ce}}$  is the number of Ce atoms in the conventional cell,  $E_{\text{bulk}}^{\text{TM}}$  is the energy of the conventional cell of TM, and  $N_{\text{bulk}}^{\text{TM}}$  is the number of TM atoms in the conventional cell.

The O<sub>v</sub> formation energy of the TM-doped CeO<sub>2</sub> surfaces was calculated by means of formula (2):

$$\Delta E_{\text{O}_v} = E_{\text{O}_v} - E_{\text{TM-slab}} + \frac{1}{2}E_{\text{O}_2} \quad (2)$$

where  $E_{\text{O}_v}$ ,  $E_{\text{TM-slab}}$ , and  $E_{\text{O}_2}$  are the total energies of the TM-doped CeO<sub>2</sub> surfaces with oxygen vacancies, the TM-doped CeO<sub>2</sub> surfaces, and the gas-phase O<sub>2</sub> molecule, respectively.

Subgroup discovery (SGD) was performed using the RealKD package.<sup>40</sup> Each feature was split into 14 subsets using a 14-means clustering algorithm.<sup>41</sup> The candidate subgroups were built as conjunctions of the obtained simple inequalities. The main idea of SGD is that the subgroups are unique if the distribution of the data they contain is as different as possible from the data distribution in the whole sample. Detailed information about the SGD approach can be found in the ESI.†

## 3. Results and discussion

### 3.1 Sure independence screening and sparsifying operator

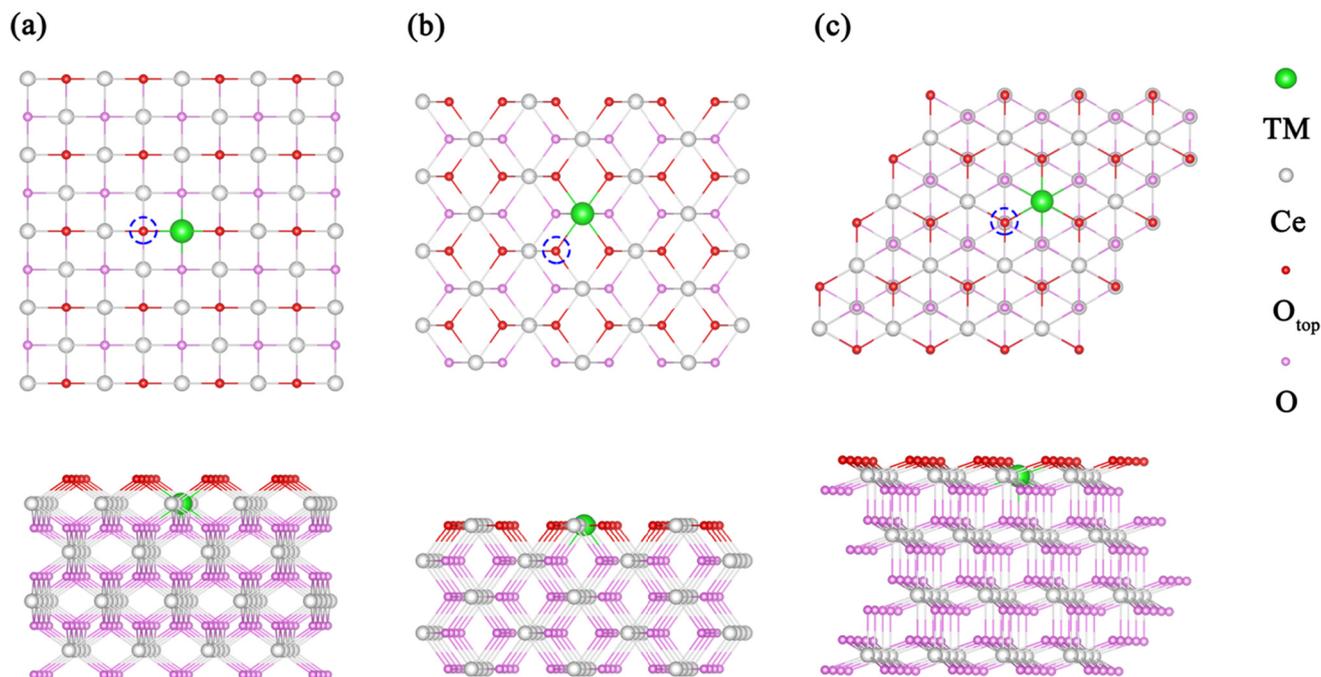
The stability of catalysts is as significant as their catalytic performance. To begin, we conducted a comprehensive investigation into the stabilities of 97 TM-doped ceria systems, including those of CeO<sub>2</sub>(100), CeO<sub>2</sub>(110), and CeO<sub>2</sub>(111). We



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the surface phase diagram of elemental and alloy transition metals under realistic conditions, the design of high-performance heterogeneous catalysts for water–gas shift and CO oxidation reactions, and machine learning-guided high-performance materials design.



**Fig. 1** Structural models of the TM-doped ceria systems. The dopant is positioned at the top cerium site of the (a)  $\text{CeO}_2(100)$ , (b)  $\text{CeO}_2(110)$ , and (c)  $\text{CeO}_2(111)$  surfaces. The oxygen vacancy sites under consideration are highlighted with dashed circles.

considered 30 different d-block TM dopants. As shown in Fig. 1, the TM dopants were positioned at the surface cerium sites of the ceria substrates. The formation energies of the TM-doped ceria systems are collected in Tables S2–S4.† Given the existence of multiple localizations of  $\text{Ce}^{3+}$  polarons,<sup>42</sup> we have taken care to include a variety of  $\text{Ce}^{3+}$  polaron configurations in our dataset to ensure that our analytical learning approaches adequately capture these features (refer to Fig. S1†).

To evaluate the impact of TM dopants on the stability of various TM-doped ceria systems, we systematically explored the correlations between the formation energies of the TM-doped ceria systems (the property) and the characteristics of the dopants (the features) using analytical learning techniques. The proper selection of initial features is of paramount importance in analytical learning. The guiding principles for initial feature selection are as follows: (a) the features can be obtained or calculated in convenient ways and (b) the features are already evaluated and shown to have close correlations with properties investigated either experimentally or theoretically. We considered two classes of features: fourteen atomic features and five system-based features, and the selection of features is based on their relevance to the properties and simplicity,<sup>43–49</sup> as detailed in Table 1. The Pearson's correlation coefficient matrix among the considered features of the TM-doped ceria systems was checked first, with the results summarized in Fig. 2a–d. The results reveal that certain features, including Ndsm, Ndm, Mm, and Rm, are closely correlated with each other for the subgroup data set encompassing 3d-, 4d-, and 5d-block metals (Fig. 2a–c). However, their corre-

**Table 1** The nineteen considered features of the TM dopants

Class	Name	Abbreviation
Atomic	First ionization energy (eV)	EIm
	Highest occupied molecular orbital (eV)	Hm
	Lowest unoccupied molecular orbital (eV)	Lm
	Atomic radius (empirical) (Å)	Rm
	Bond dissociation energy of homo-diatom molecules (eV)	BDEm
	Cohesive energy (eV)	ECm
	Radius of the s-orbital (Å)	RSm
	Radius of the d-orbital (Å)	RDm
	Electronegativity	ENm
	Number of d valence electrons	Ndm
	Total number of d and s valence electrons	Ndsm
	Miedema parameters (volt)	MdLm
	Miedema parameters (density unit)	MdNm
	Relative atomic mass (a.m.u.)	Mm
System	Bader charge of the dopant ( $e^-$ )	$q$
	Fermi level (eV)	FL
	Work function (eV)	WF
	d-band center of the dopant (eV)	DC
	p-band center of oxygen (eV)	PC

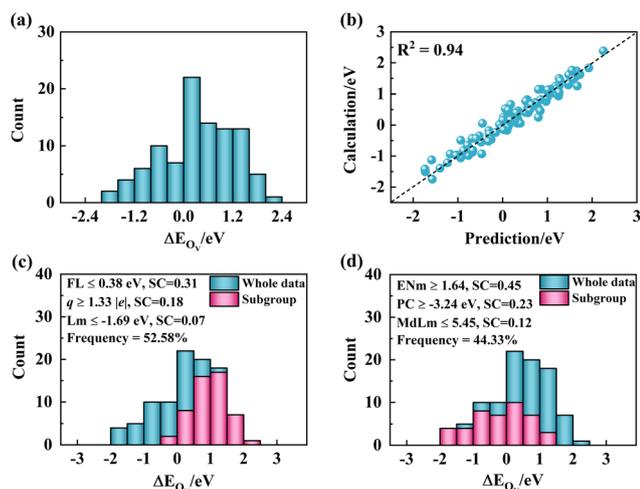
lation significantly diminished for the entire data set comprising all d-block metals (Fig. 2d). This observation suggests a high degree of diversity within the primary feature space, which is well-suited for subsequent analytical learning analyses.

An in-depth investigation was conducted to explore the correlations between the primary features and the formation energies of the TM-doped ceria systems. The findings are presented in Fig. 3 and Fig. S2,† which reveal that the formation energies



**Table 2** Components of descriptors and their coefficient (C) of the multi-task SISSO-identified best model. The intercept values are  $-1.20$  for  $\text{CeO}_2(100)$ ,  $2.84$  for  $\text{CeO}_2(110)$ , and  $-3.96$  for  $\text{CeO}_2(111)$

Descriptor	$\text{CeO}_2(100)$ (Task 1) C1	$\text{CeO}_2(110)$ (Task 2) C2	$\text{CeO}_2(111)$ (Task 3) C3
$(\text{MdLm} - \text{WF})/(q \times \text{ENm}) - (\text{WF}/\text{MdLm})$	$-0.19 \times 10^1$	$0.32 \times 10^1$	$-0.53 \times 10^1$
$(\text{Mm}/(\text{DC} + \text{BDEm})) / (\text{FL} + (\text{MdLm}/\text{ECm}))$	$-0.20 \times 10^{-4}$	$0.58 \times 10^{-5}$	$-0.40 \times 10^{-3}$
$(\text{WF}/\text{Lm}) / ((\text{Rm} \times \text{MdLm}) - (\text{WF}/\text{RDm}))$	0.71	-0.16	$0.38 \times 10^{-1}$
$(q + \text{Ndm}) / (\text{MdLm} - \text{EIm} - (\text{Ndm}/q))$	$-0.19 \times 10^{-1}$	$-0.74 \times 10^{-1}$	$-0.27 \times 10^{-1}$
$(\text{MdNm}/(\text{MdNm} - \text{RSm})) / (\text{DC} + \text{WF} - \text{RSm})$	$0.47 \times 10^{-2}$	$0.32 \times 10^{-2}$	$-0.66 \times 10^{-3}$



**Fig. 4** Analytical learning of surface  $\text{O}_v$  formation energies of the TM-doped ceria systems. (a) The histogram distribution of data samples for  $\text{O}_v$  formation energies of the TM-doped ceria systems, (b) the error distribution between the SISSO model predicted energies and DFT calculated energies for the TM-doped ceria systems, and the results of the SGD by maximizing (c) and minimizing (d) the surface  $\text{O}_v$  formation energies.

### 3.2 Subgroup discovery

The components of the optimal model identified by the SISSO approach are presented in Table 2. Additionally, Fig. 4 displays the error distribution of the  $\text{O}_v$  formation energies as predicted by the optimal SISSO model (Fig. 4b), alongside the distribution of the  $\text{O}_v$  formation energies themselves (Fig. 4a). While the SISSO model provides mathematical formulas, gaining a deeper understanding of the mechanisms underlying the formation of  $\text{O}_v$ s in various TM-doped ceria systems using the SISSO model remains a challenging task. In an attempt to identify the key descriptive parameters and facilitate a physical understanding of the actuating mechanisms, we applied the SGD local artificial intelligence approach.<sup>32</sup> SGD is a method designed to identify local patterns in data that maximize a specific quality function. The identified pattern/subgroup is defined as an intersection of simple inequalities involving provided features.<sup>50</sup> The so-called quality function measures the degree of distinctiveness of a pattern/subgroup in comparison to the entire data set (further

details about the implementation of the SGD approach can be found in the ESI†).

To gain better insight into the factors and mechanisms that facilitate the formation of  $\text{O}_v$ s on various TM-doped ceria systems, we utilized the SGD approach. Starting with the identification of subgroups that maximize the  $\text{O}_v$  formation energies, one specific subgroup was singled out. This subgroup, which consists of 51 data points or 52.58% of the total dataset as depicted in Fig. 4c, was distinguished by the conditions  $\text{FL} \leq 0.38$  eV,  $q \geq 1.33$  |e|, and  $\text{Lm} \leq -1.69$  eV. On the other hand, the identification of subgroups that minimize  $\text{O}_v$  formation energies led to the discovery of another subgroup. This subgroup contained 43 data points or 44.33% of the total dataset as shown in Fig. 4d, and was characterized by the conditions  $\text{ENm} \geq 1.64$ ,  $\text{PC} \geq -3.24$  eV, and  $\text{MdLm} \leq 5.45$ . The importance of each feature was determined by its respective support score (SC), which is derived from the quality function value ( $Q$ ). A score of 0 suggests that removing this specific feature does not affect the value of  $Q$ , indicating that this feature does not influence the SGD result. Among these features,  $\text{FL} \leq 0.38$  eV and  $q \geq 1.33$  |e| stood out for their relatively high SCs, which the SGD approach identified as key in inhibiting  $\text{O}_v$  formation. In contrast, features  $\text{ENm} \geq 1.64$  and  $\text{PC} \geq -3.24$  eV were noted to facilitate  $\text{O}_v$  formation. In a physical context, a lower Fermi level ( $\text{FL} \leq 0.38$  eV) implies that the highest occupied 2p orbitals of lattice oxygen should be situated at relatively low energy levels. As a result, electron transfer from the removed neutral oxygen to the empty d-orbitals of the TM dopants or the f-orbitals of the lattice cerium site becomes less feasible, inhibiting surface  $\text{O}_v$  formation. Similarly, the condition  $q \geq 1.33$  |e| can be interpreted from the fact that four positive charges ( $4e^+$ ) are retained when one neutral cerium atom is removed. If these positive charges are not adequately compensated by the TM dopant (as can occur when the  $q$  is small), the remaining positive charges will form empty hole states that can combine with the electrons left after oxygen removal, thereby facilitating  $\text{O}_v$  formation. Thus, a larger  $q$  is crucial to suppress  $\text{O}_v$  formation. Furthermore, a larger dopant electronegativity ( $\text{ENm} \geq 1.64$ ) and a larger p-orbital center ( $\text{PC} \geq -3.24$  eV) of the lattice oxygen can facilitate  $\text{O}_v$  formation. Dopants with lower electronegativity, due to their large electronegativity difference, bind strongly with the lattice oxygen, inhibiting  $\text{O}_v$  formation. On the other hand, a higher p-orbital center eases the electron transfer from oxygen

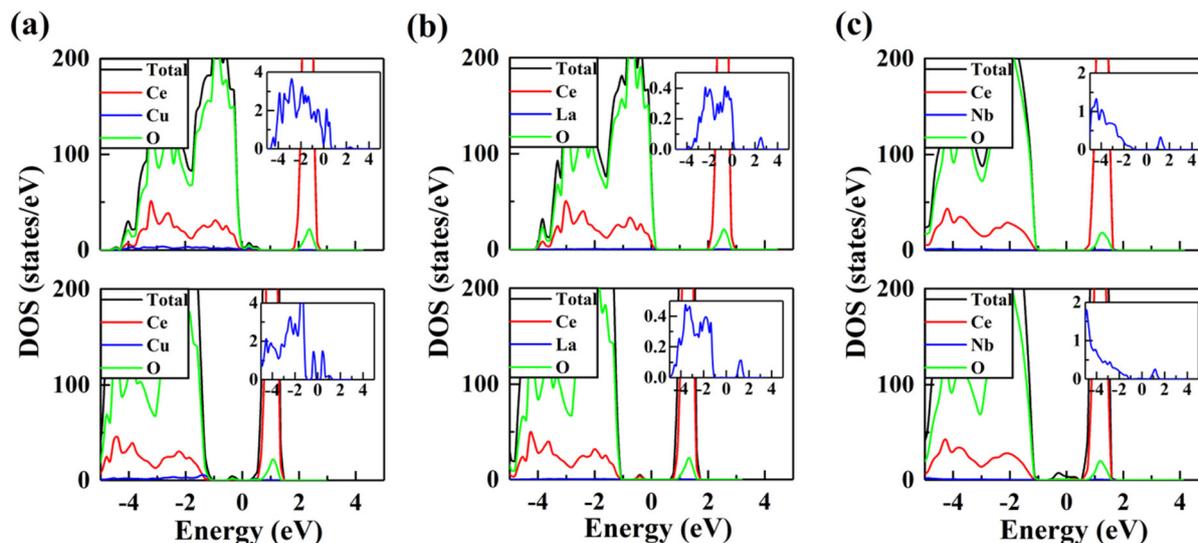


Fig. 5 Species projected density of states for surface doped  $\text{CeO}_2(111)$  surfaces. The TM-doped  $\text{CeO}_2(111)$  surfaces with low  $O_v$  formation energy (a, Cu doping), moderate  $O_v$  formation energy (b, La doping), and high  $O_v$  formation energy (c, Nb doping).

to TM sites upon oxygen removal, promoting  $O_v$  formation. In addition, the insights gleaned from the SGD analysis are applicable to other transition metal-doped metal oxides as well (Table S7<sup>†</sup>). With the help of SGD, a sophisticated understanding was developed that would have been challenging to achieve without local artificial intelligence. SGD has proven useful in identifying multiple alternative subgroups, each corresponding to different mechanisms affecting the target properties. The target properties with the desired values that lie in a specific range are also factors affecting the identified subgroups.<sup>51</sup> Exploring the role of different factors can significantly improve the interpretability of the subgroups.

The interpretation of SGD results is sometimes limited by our domain knowledge. To validate the abovementioned explanations, we further analyzed the species projected density of states of three representative  $\text{CeO}_2(111)$  systems with low (Cu-doped), moderate (La-doped), and high (Nb-doped)  $O_v$  formation energies (Fig. 5). For the Cu-doped surface, pronounced 3d empty states of Cu exist near the Fermi level due to the relatively large  $q$  of Cu ( $-1.10 e^-$ ) (Fig. 5a). These empty states will be occupied by extra electrons to facilitate the removal of neutral oxygen and the formation of  $O_v$ s. For the Nb-doped surface, there are no empty d-orbitals near the Fermi level due to the relatively small  $q$  of Nb ( $-2.58 e^-$ ). The electrons remaining after the removal of neutral oxygen must occupy the 4f states of the cerium atoms, splitting from the stable unoccupied 4f states of cerium atoms, which makes  $O_v$  formation difficult (Fig. 5c). The density of empty states decreases in the order of Cu-doped > La-doped (Fig. 5b) > Nb-doped surfaces, resulting in  $O_v$  formation energies that increase in the order of Cu-doped < La-doped < Nb-doped surfaces. Similar findings were observed for both the  $\text{CeO}_2(100)$  and  $\text{CeO}_2(110)$  systems.

## 4. Conclusions

In summary, by synergistically utilizing first-principles calculations and an interpretable artificial intelligence approach, we have successfully identified the key descriptive features and mechanisms that facilitate the formation of oxygen vacancies in various transition metal-doped  $\text{CeO}_2$  systems. The Fermi level of the system and the electronegativity of the dopants are the paramount parameters (features) influencing the formation of oxygen vacancies. By integrating domain knowledge, symbolic regression, subgroup discovery, and electronic structure analysis, the facilitated formation mechanism of oxygen vacancies was attributed to the distributions and behaviors of the occupied 2p states of lattice oxygen and the empty states of the transition metal dopants near the Fermi level. Our methodology can be easily adapted to other transition metal oxide-based functional materials. It demonstrates the powerful potential of artificial intelligence to provide new understanding and insights into the physical principles underlying data.

## Conflicts of interest

There are no conflicts to declare.

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