Insights of cation ordering in double perovskites oxides from machine learning

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This work investigates origins of cation ordering of double perovskites using first-principles theory computations combined with machine learning (ML). We have considered various possible oxidation states of A, A’, B and B’ from the family of transition metal ions to construct datasets. A conventional framework employing traditional ML classification algorithm such as Random Forest (RF) combined with appropriate features including geometry-driven and key structural modes leads to highly accurate prediction (∼98%) of A-site cation ordering. This study evaluates accuracy of ML models by entailing analyses of decision paths, assignments of probabilistic confidence bound, and finally introducing a direct non-Gaussian acyclic structural equation model to investigate causality. A comparative study of utilization of first-principles driven features versus those computed with lower fidelity is added to further elucidate the role of structural modes for accurate prediction of cation ordering in double perovskites.

I. INTRODUCTION

Cation ordered double perovskites of the form AA’BB’O₆ with A as an alkaline-earth or rare-earth ion, B and B’, as transition metal ions, exhibit a wide range of properties due to their structural and compositional flexibility[1, 2]. In particular, a substantial number of compounds within this family of materials as reported by both theoretical and experimental studies, show multiferroic and polar metallic behavior[3–7]. In AA’BB’O₆, the BB’ sublattices typically order in rock-salt while AA’ sublattice can order in layered [L], rock-salt [R] or columnar [C] ordering leading to diverse structural, electronic and magnetic properties[8–10]. Fixing BB’ as rock-salt while considering all three possible AA’ orderings such as AA’ layered (A[L]B[R]) ordering and AA’ rock-salt ordering (A[R]B[R]) lead to non-centrosymmetric space group (P2₁ and Pc, respectively), if (a–a–c⁺) distortion is imposed. Here, (A[L]B[R]) ordering is of particular interest due to the microscopic polarization arising because of non-cancelation of layered polarization in two successive AO and A’O layers. The low symmetry phase is established by hybrid improper ferroelectric (HIF) mechanism[11–17]. The central question still remains as how to achieve A-site cation ordering in double perovskites.

The disorder tendency at A-sites is more pronounced than B site. Consequently, B-site cations tend to order more efficiently compared to the A-sites. To form stable A/A’ ordering, B/B’ rock-salt ordering coupled with second order Jahn-Teller (SOJT) distortions at the B’ site (i.e., placement of d⁰ cations at the B’ sites) is known to be the most crucial factor[18]. In general, a clear ordering (irrespective of A-site and B-site ordering) is reported to be dependent on a variety of parameters. A non-exhaustive list of such factors include differences in cation radii and/or oxidation states, charge ordering, cooperative first order Jahn-Teller distortions of B cations (FOJT), A-site vacancies coupled with SOJT distortion, tilt of BO₆/B’O₆ octahedra. Other physical properties, structural modes, oxidation states, coordination, tolerance factor, external conditions and complex interplay between them can also play important roles in this context. However, full or partial dependence of these factors can not be fully understood by sole exploitation of density functional theory (DFT)-based methods. Consequently, it creates a unique opportunity to evaluate if data-driven and ML techniques can help to solidify such understandings.

In this work, we have employed DFT computations and supervised traditional machine learning (ML) techniques to explore such insights. Different possible oxidation states of A, A’, B, B’ with B, B’ elements belonging to 3d-3d, 3d-4d and 3d-5d blocks, are considered to construct datasets ranging over a wide compositional space. To design a robust set of descriptors, both DFT-derived and non-DFT derived features are taken into consideration. While the first contains information retrieved directly from the first-principles computations, the latter relies on independent (computed using non-expensive physical models) representation of structures and order parameters. The models based on non-DFT features provide the user an alternative to obtain a reasonable prediction of cation ordering in the absence of accessibility to more robust DFT-driven features. Comparison between these two type of models, as included in this work, also gives a measure of importance of the DFT-driven features for deriving reliable predictions.

Multiple variations of the parent dataset are created to
carefully examine the role of the entire descriptors space driving the cation ordering and corresponding energy differences between different types of ordering. A series of classification and regression models are constructed utilizing a decision tree-type RF algorithm[19]. While a set of models perform multi-label classification into columnar (0), layered (1) and rock-salt (2) ordering, other models predict distinguished labels signifying formation of clear layered ordering (0 or 1). These models show high accuracy (balanced accuracy scores >94%) for both classification and regression models. The accuracies vary between choice of descriptors between DFT and non-DFT features.

Reasonable predictions of cation ordering along with providing signatures of driving factors for cation ordering can be achieved utilizing such ML models. However, if we would like to understand what is causing the cation ordering to be of a specific kind, for e.g., columnar versus rock-salt and how one feature can affect the other leading to the target, assessing linear or non-linear correlations are not enough. In addition, from the overall accuracy score, it is hard to determine if all systems present in the dataset are being predicted accurately with the same confidence bound. Hence, we have established methodologies to systematically address these potential caveats present in conventional ML frameworks deeming interpretability. We have assigned probability estimates as confidence bounds for each system by considering decisions made by each decision tree in RF. These also indicate existence of possible competing phases of structures which are explained in detail as a part of the study. Next, from the combination of identified important descriptors, SISSO (sure independence screening and sparsifying operator) method [20–22] is implemented to explore if functional forms of these primary descriptors can be formulated into linear equations to quantify the feature dependencies. We have also visualized the decision paths (representative case can be found in Supplementary Material) to open up the black-box of ensemble of trees to show the importance of competing features regulating the predictions of the models. Finally, direct linear causal networks are built to study existing structure-property relationships going beyond the standard practices of correlation. Such models delineate how multiple features are causally related, can be tuned in different possible combinations, as a result of which, the target property, such as cation ordering, can be observed or modified.

The key stages of the entire framework involving dataset compilation using DFT computations, evaluation of descriptors space, construction of interpretable ML models, assessment of functionalized features and causality has been illustrated in Figure 1. All details about the associated methodologies can be found in the Methods section. Overall, this DFT-based study com-
FIG. 2. **Representation of double perovskites of interest** (a) Structural illustrations of various A-site cation orderings such as A-site layered, A-site columnar and A-site rock-Salt with B-site fixed as rock-salt ordering. The magnetic configuration considered here is of G-type AFM ordering. (b) Distribution of the data set in terms of various possible oxidation states available for BB’ sites such as (2,6), (4,2), (4,3)/(3,2) and (4,4), respectively. (c) The number of entries present in the dataset if the charge states of AA’ vary as (1,3), (2,4), (2,3)/(2,4) and (3,3), respectively. The variations of the charge states for the systems are plotted here with respect to ranges of tolerance factor.

combined with causal ML models provides a comprehensive understanding of the determining factors behind cation order ordering exhibited by double perovskites.

II. RESULT AND DISCUSSIONS

A. Datasets & Descriptors

Dataset construction: To construct the dataset, we have studied various pairs of transition metal ions placed at A, A’, B and B’ cation sites. All 3d, 4d, 5d block elements are selected and combined based on their corresponding charge states. In a formula unit cell of AA’BB’O₆ double perovskites, the oxidation states of A, A’, B and B’ should sum up to +12. Figure 2(a) illustrates the structures of three A-site cation orderings with B-site kept fixed as rock-salt ordering with G-type antiferromagnetic (AFM) configuration. The distribution of all 410 entries in the dataset are plotted with respect to variations in the tolerance ranges. In Figure 2(b) this distribution is shown for different oxidation states for BB’ sites, as (2,6), (3,2), (4,2), (4,3) and (4,4), respectively. For AA’, the possible oxidation states become (1,3), (3,4), (2,2), (3,2) and (4,4) as represented in Figure 2(c). The charge differences (CD) between B and B’ thus evaluated are 4, 1, 2 and 0, whereas, CD between A and A’ are 2, 1 and 0, respectively. As an example, for a CD of 2 between A, A’, where A is Na(+1) and A’ is Y(+3), a total of 176 systems are considered assuming the CD between B, B’ is 4 (with in 3d-5d elements). Out of all transition metal ions after mixing elements from different blocks, the total number of compounds that are considered from the combinations of 3d-3d, 3d-4d and 3d-5d are 224, 10 and 176, respectively. This gives rise to a dataset consisting a total of 410 entries. Next, we have performed geometry optimization utilizing DFT within GGA+U approximation to obtain the relaxed structures. The self-consistent energies are then evaluated for the three types of cation ordering for all individual compounds present in the dataset. For each compound, there are three entries corresponding to the three types of ordering. The labels such as 0, 1 and 2 are assigned based on the initial and final structural configurations associated with the same. For a compound entry with label 2 for example, the final structure of the compound must resemble the template of A-site rock-salt ordering as shown in Figure 2 (a). A subset of this dataset is also chosen to examine the formation of clear layered ordering. For this case, a cut-off energy difference of -32 meV is set. The reference energy to evaluate the energy difference between various orderings and assigning corresponding labels, is always considered to be of the layered ordering. For example in the later subset
FIG. 3. **Representation of structural modes and corresponding distributions** Key structural modes such as in-phase rotation ($Q_{R+}$), tilt ($Q_T$), antiferroelectric A-site displacement ($Q_{AFE-A}$), 2-dimensional charge disproportionation (CD$_{2D}$), 3-dimensional charge disproportionation (CD$_{3D}$) and antiferroelectric O-site displacement ($Q_{AFE-O}$), as computed for the systems are illustrated in (a-f), respectively. In case of out-of-phase rotation (not shown here), the in-plane oxygen atoms located at both top and bottom layers of BO$_6$ (or B’O$_6$) octahedra rotate in the opposite directions. The 2D kernel-density plots (g-k) are utilized here to show different amplitudes of structural modes with respect to three types of A-site cation ordering. The distribution of $A'_{\text{dis}}$ is also plotted (l) here.

TABLE I. List of all models with descriptors and targets as constructed in this work. All features related to energy such as ground-state energy, energy per unit cell are excluded from the list."*

| Model | Number of entries in dataset | Features | Target |
|-------|-------------------------------|----------|--------|
| I     | 410                           | Geometry-driven | 0, 1 or 2 |
| II    | 194                           | Structural modes | 0, 1 or 2 |
| III   | 165                           | Geometry-driven & structural modes | 0, 1 or 2 |
| IV    | 108                           | Geometry-driven | 0 or 1 |
| V     | 100                           | Geometry-driven & structural modes | 0 or 1 |
| VI    | 100                           | Geometry-driven* & structural modes | Energy difference |
| VII   | 100                           | structural modes | Energy difference |
| VIII  | 165                           | non-DFT derived features | 0, 1 or 2 |
| IX    | 100                           | non-DFT derived features | 0 or 1 |

of data entries, if the energy difference between layered and columnar or rock-salt for a compound is above -32 meV, the compound is assigned to label 1. This choice is driven by the fact that double perovskite systems most-likely exhibit clear layered ordering as validated by experimental observations.[23, 24] In addition, this specific cut-off energy difference also complies with previous DFT-based investigation [25] that reports formation of cation-ordered polar phases based on such criteria. The distribution of the compositional space as shown in Figure 2 represents a wide range of charge distributions of the cation sites. In addition, this compositional span also encompasses a broad variety of structures ranging from cubic to orthorhombic as quantified by the differences in tolerance factors. Consequently, this leads to notable changes in geometry-driven features and struc-
FIG. 4. Confusion matrices to represent classifications of ordering. Classification results as described by confusion matrices for the training (a, c, e, g) and test (b, d, f, h) sets for Model III, VI, VIII and IX, respectively. Model III, VIII use multi-label RF classification to predict columnar, layered, rock-salt ordering while for Model VI and IX, it is a binary classification task to categorize systems in presence or absence of clear layered ordering.

Structural modes which are considered as key descriptors in the construction of ML models.

**Geometry-driven features**: The geometry-driven features such as charge states ($C_A, C_{A'}, C_B, C_{B'}$), coordination numbers ($Cn_A, Cn_{A'}, Cn_B, Cn_{B'}$), ionic radii ($r_A, r_{A'}, r_B, r_{B'}$), average ionic radii ($\langle AA'_{avg}, BB'_{avg} \rangle$), tolerance factors (TF), optimized energies (Energy), Fermi occupation numbers ($Cn_p, Cn_{A}, Cn_{A'}$), electronic bands, magnetic moments (total mag), individual magnetic moment ($mag_B, mag_{B'}, mag_B'$), s, p, d occupancies at all cation sites ($A_s, A_p, A_d, A'_{s}, A'_{p}, A'_{d}, B_s, B_p, B_d, B'_{s}, B'_{p}, B'_{d}$), antiferroelectric displacements of A, A' sites ($A_{\text{dis} x}, A'_{\text{dis} x}, A'_{\text{dis} y}, A'_{\text{dis} y}$) along x, y directions, tilt ($\theta_{\text{tilt}}$) and rotation ($\theta_{\text{rot}}$) angles are first included in the descriptors space. All of these features are obtained utilizing the information given by the initial structures followed by the optimized ones within the evaluations using first-principles computations.

**Structural modes**: The next segment of features space comprises of key structural modes. Bulk double perovskites undergo phase transition from high symmetry to low symmetry driven by unstable phonon modes, as temperature is lowered. The modes driving any specific property is referred to as functional mode. Either single or multiple modes can be responsible for transition from high symmetry to low symmetry phase. Hence, these modes are also proven to be well representation of existing structural distortions, rotations, tilts between different planes or octahedra cages, Coulomb interactions, and even charge disproportionations arising due to changes in bond lengths, volumes of B or B'O$_6$ octahedra. Below we provide a brief description of all modes that are included in this study. The key structural modes for the double perovskites are namely in-phase rotation ($Q_{R+}$), tilt ($Q_T$), out-of-phase rotation ($Q_{R-}$), antiferroelectric A-site displacement ($Q_{\text{AFE}A}$), antiferroelectric O-site displacement ($Q_{\text{AFE}O}$), 2-dimensional charge disproportionation ($CD_{2D}$) and 3-dimensional charge disproportionation ($CD_{3D}$). The structural modes are shown in Figure 3(a-f). The $Q_{R-}$ and $Q_{R+}$ modes arise due to rotations of apical in-plane oxygen atoms located at both top and bottom layers of BO$_6$ (or B'O$_6$) octahedra in the same and opposite directions, respectively. These modes exist in the ab-plane. $Q_T$ in bc plane comes into play when the oxygen atoms from the top and bottom layers of BO$_6$ (or B'O$_6$) octahedra move in the same direction. The displacement of the A and A'-sublattices occur in opposite direction. The ionic radii of A and A' are different. Consequently, it gives rise to a ferrielectric (FIE) distortion, very often known as anti-ferroelectric A-site displacement ($Q_{\text{AFE}A}$) mode in the literature. This mode is described along the b-axis. For anti-ferroelectric O-site displacement mode, $Q_{\text{AFE}O}$ planar O-atoms are displaced towards the higher charge state due to electrostatic Coulomb's interaction. The volume of B'O$_6$ typically increases while the same for the BO$_6$ octahedra.
dra gets reduced. This effect is quantified by the CD$_{3D}$ mode. For CD$_{2D}$ mode, the bond lengths between BO increase in one direction and reduce in another. The B’O bond lengths overturn the effect of BO bond lengths. The amplitudes of all of these modes are computed within the DFT regime (details included in Methods section) and used to construct ML models combined with the geometry-driven features.

Figure 3(g-k) shows continuous distributions of the amplitudes of structural modes spanning over the full compositional space. It is evident from Figure 3(g) that Q$_T$ is absent for compounds with C-type ordering. This is due to the fact that in case of C-type ordering, oxygen atoms are located at the centre of the symmetry and can not be moved towards a particular A cation site. Presence of CD$_{3D}$ (h) is required to exhibit R-type cation ordering. This mode is missing in C and L-type orderings since they are are confined in two dimensions and therefore, only CD$_{2D}$ mode becomes relevant. The average amplitudes of QA$EFE$A (Figure 3(i)) modes for C, L or R-type of orderings are in the same order of magnitude such as $\sim$1.91Å. CD$_{2D}$ modes (Figure 3(j)) are only present for C or L-type of ordering as discussed. QA$EFE$O (Figure 3(k)) is suggestive of formation of L-type of ordering. Charge separation between AO and A’O layers is responsible for QA$EFE$O. This mode is missing for C and R-type orderings which can also be confirmed by analysis of the structural mode. In this mode, the in-plane oxygen atoms move towards the smaller A-site cations (generally one with the higher oxidation state) to satisfy the bonding/coordination environment. The region with high amplitudes of A’ displacement corresponds to rock-salt whereas for the other two types of ordering, these magnitudes are minimal. Moreover, from similar analyses of the datasets, we can also claim that Q$_{R-}$ is present for all compounds exhibiting only C-type of ordering. Thus, Q$_{R-}$ becomes extremely important among other features to determine the presence or absence of C-type ordering. The average amplitudes of Q$_{R+}$ modes for C, L or R-type of orderings are in the same order of magnitude such as $\sim$ 1.08Å.

Overall, if we consider the uniqueness of the structural modes to describe L, C or R, we can emphasis on the following points:

(a) QA$EFE$O, Q$_{R-}$, CD$_{3D}$ modes are only present in L, C and R ordering, respectively and
(b) Q$_T$ and CD$_{2D}$ modes are only absent in C and R ordering, respectively.

Hence, these information on the structural modes can play an important role in classifying L, C or R-type orderings.

Non-DFT derived features

Even though it is straightforward to get an estimate for most of the geometry-driven features utilizing the results from the converged computations, decomposing the phonon modes can be challenging depending on the structural complexity. In addition, the computations may turn out to be expensive. For elements for which reliable PAW potential may not be available, these features can not be obtained. Thus ML models solely dependent on DFT-derived features are not enough to find a generalized model to predict cation ordering. As an alternative, we have computed an additional set of descriptors using Automatminer [26] to include material representations of complementary features of the DFT-derived ones. This evaluation as further discussed later in the section, also leads to interesting observations stating how reliable our predictions are if we vary the features spaces for different compounds.

B. ML models

The RF classification and regression algorithms are employed to construct the ML models. The choice of RF, in comparison to other classification or regression algorithms, is driven by its performance in the previous studies [27, 28] when applied to datasets of small size, as well as its capability to rank utilized descriptors by importance. This feature of the RF algorithms is proved to be essential for investigations where underpinning physical properties driving the target is important. We have considered ensemble of trees to perform the task of classifying cation ordering or predicting energy differences to form different types of ordering. Once the optimized models are constructed based on the best set of hyperparameters after performing grid-search, the feature importances are assessed to rank them based on their respective importances. The feature importance score produced by RF represents the decrease in the weighted impurity over all trees for every feature. These selected features are then used in the subsequent explorations to investigate effects of functionalized descriptors using SISSO and existing causal ordering and strengths.

RF models: We have built a series of models by considering different combinations of the features space. The classification task is to either categorize compounds into (a) three types of cation ordering (0, 1 or 2), or into (b) clear layered ordering (0 or 1). Energy difference to form clear layered ordering is predicted by the regression models. A complete set of list of the models with corresponding brief descriptions can be found in Table I. Figure 4 represents the results of the best classification models for both training and test sets to predict cation ordering. The number of compounds for which the predicted classes match the true classes is represented by the diagonal elements of the confusion matrix. From the plots, it is evident that all four models as constructed by DFT-derived (a-d) and non-DFT derived features (e-h) perform well. The balanced accuracy scores (training, test) for these models are (1.0, 1.0), (1.0, 0.96), (0.96, 0.73) and (0.88, 0.85), respectively. For predicting C, L or R-type of orderings, features such as CD$_{3D}$, QA$EFE$A, Q$_{R-}$, Q$_T$, QA$EFE$O, Q$_T$, A’$\text{dis}^x$ turn out to be the most important. Formation of clear layered ordering can be tied to descriptors such as $E_{\text{diff}}$, $r_{D'}$, $C_{A'}$, $C_{B'}$, A’$\text{dis}^y$. For
TABLE II. List of the five most important descriptors for selected classification and regression models.

| Model Type | Features (in order of descending importance) |
|------------|---------------------------------------------|
| II multi-label classification | CD, $Q_{AF EA}$, $Q_{R-}$, $QT$, $Q_{AF EO}$ |
| III multi-label classification | CD, $Q_{T}$, $A'_{dis}x$, $Q_{AF EO}$, $CD_{2D}$ |
| V binary classification | $E_{diff}$, $r_{B'}$, $C_{A}$, $C_{B}$, $A'_{dis}y$ |
| VI regression | $C_{B}$, $r_{B'}$, $B'_{p}$, $B'_{d}$, $A'_{dis}y$ |

**FIG. 5. Mean probability estimates for predictions** The mean probability scores (discrete as illustrated by box plots) and associated densities (continuous as illustrated by violin plots) are shown for the training (a, c, e, g) and test (b, d, f, h) sets for Model III, VI, VIII and IX, respectively. These models are built with DFT (a-d) and non-DFT-derived (e-h) features to predict columnar, layered, rock-salt and clear layered ordering.

Predicting energy differences that determines the formation of clear layered ordering, all DFT-derived features related to the energy of the systems are discarded from the descriptors space to avoid any redundancy. We show in Table II, that $C_{B}$, $r_{B'}$, $B'_{p}$, $B'_{d}$, $A'_{dis}y$ features drive the decision if a system can exhibit clear layered ordering. This regression model shows $R^2$ of 0.93 signifying reasonable accuracy.

Within the regime of non-DFT derived features, components of the sine Coulomb matrix representing the electrostatic interactions along with the structural complexity are crucial to classify systems into C, L or R-type of ordering. The structural complexity [26] per atom is defined as the summation over the ratio of all inequivalent sites to total sites present in the unit cell, multiplied by the logarithm of the same ratio. For prediction of clear ordering, $p$, $d$ occupancies at the cation sites along with the total number of valence electrons turn out to be important. We note, that these features carry full or partial information as described by the first-principles based ones. Thus, these counterparts are complimentary to DFT-derived ones for systems for which DFT results become inaccessible due to either expensive nature of the calculations or unavailability of appropriate potentials.

Although construction of reasonably accurate models are possible even using these set of descriptors, it is clear that the utilization DFT-derived features capture the formation of cation ordering better. The classification of C[0], L[0] and R[2] is dependent both on the presence or absence of specific structural modes in the system as well as on their amplitudes. In addition, these functional modes as driven by symmetry also affect cation displacements, cell parameters. The rearrangement of cations in the lattice, mismatch between cation sizes are also crucial for exhibition of a particular type of A-site cation ordering. All such information can only be well-captured by DFT computations with great accuracy. Hence, the DFT-derived features turn out to be more relevant here.

However, even though the classification models have high overall accuracy, not all trees in the ensemble of trees may lead to same decision. Furthermore, not all the systems can be predicted with same accuracy even within the same model as well as if the features space is varied. Thus, there is a need to assign a more rigorous confidence
bound as compared to using the standard accuracy measures. Here, we compute the mean probability scores or density where discretized probability scores should add up to 1, for three (or two for binary classification) different classes for the multi-label classification models. The results are represented by overlaid box and violin plots shown in Figure 5 for the training (a, c, e, g) and test (b, d, f, h) sets of Models III, VI, VIII and IX, respectively. The box plots represent the discretized probability scores for all classes. These scores vary between 0 and 1. The violin plots represent continuous distributions of probability density estimates. The width of these segments show that the confidence levels to predict different classes vary, even within the same model. A cut-off value (0.65 is considered in this study) for the probability score can be assigned to shortlist all predictions with high accuracy. In other words, comparing these confidence bounds, it becomes easy to distinguish the samples with high prediction accuracy versus that below the cut-off. For the latter, even though corresponding confusion matrix may show a right classification, it does not indicate the possible existence of competing ordering which is now well-captured by this analysis.

One of the key observations derived from the analysis shows that for AA’BB’O₆ compounds, where A, A’, B, B’ charge states are +1, +3, +2, and +6, respectively (where B, B’ are of 3d and 5d blocks, respectively) the formation of clear layered ordering can be predicted with high probability (>0.65). However, for AA’BB’O₆ compounds with B and B’ to be +2, +4 (both B and B’ are 3d elements), the probability scores are competing, meaning high confidence level cannot be established for the predictions. This can further be explained if we look at the charge separation between AA’ that enhances the possibility of formation of clear ordering in 3d-5d systems. The 3d-5d systems energetically favor B-site rock-salt A-site layered cation ordered P2₁ phase. This phase is also of particular interest in terms of exhibition of multiferroic property in double perovskites.

To further test the robustness of the ML models, we have constructed few additional models utilizing the dataset as used in Model III. Randomly selected 13 compounds are kept aside for validation and the model is retrained using the same set of geometry-driven and structural modes features. While the training, test accuracy along with the ranking of descriptors based on importance remain the same as before, the balanced accuracy score for the validation set also comes out to be 1.0, all satisfying the probabilistic confidence bound. These are the predictions on entries that this additionally-trained model has not seen before. Thus, it implies robustness of the classification model. We note that dividing into training, test and validation for all the models are ideal. However for a small dataset as used in this study, this segregation also takes away a significant number of entries. Therefore, the validation scheme is only introduced here in a separate model to establish representative accuracy of the models. In addition, we have also assessed predictions on a dataset with 5 NaYBB’O₆ based compounds, where B = Co, Fe, Ni and B’ = Os, Re and W. Each compound in this dataset has corresponding 9 entries giving rise to a total of 45 systems. Please add why there are 41 compounds in the validation set instead of 45. However, as some of the structures are highly distorted and could not be decomposed with high confidence, hence we have used 41 systems for the validation data set. The respective cation ordered phases are CC, CL, CR, LC, LL, LR, RL, RR, where, the first letter represents the ordering of the A-site and the latter is of the B-site. All computations assume collinear spins and G-type AFM ordering for magnetic ions. Apart from the reported ones, we have also found new structural modes which are relevant for capturing ordering in these combinations. These are 2-dimensional Jahn-Teller distortion (JT₂D), 2-dimensional electronic displacement (ED₂D) and 3-dimensional electronic displacement (ED₃D), respectively (see Supplementary Material for more details). The new structural modes arise due to the new cation ordered phases in the validation set. While a low accuracy of 40-50% can be established using Model III, this performance significantly improves if the same model can be retrained with the information on these new structural

![FIG. 6. Direct causal networks](image)

Causal networks to predict three types (a, b) of cation ordering (0, 1 or 2), and (c) clear layered ordering (0 or 1) using ten most important features selected RF classification models constructed with descriptors space including both geometry-driven and structural modes.
modes. We have included additional details on these datasets and models in the Supplementary Material. The performance on the validation sets further establish the importance of functional modes and geometry-driven features to determine A-site or even B-site cation ordering for a variety of systems.

**SISSO:** SISSO method allows to introduce non-linearity into the features space by searching over functionalized descriptors. The details of this implementation can be found in the Methods section. Overall using LASSO and logistic regressions within the $l_1$ norm, optimized linear combinations of functionalized descriptors leading to the target property can be obtained. Table III gives the list of combinations of the functionalized features for datasets used in Model III and VI to classify into three types of ordering and predict energy differences to form clear layered ordering, respectively. We only choose these four models and related important features to perform SISSO since both of these models carry the most information about the DFT-derived features. While combination of the descriptors may lead to the target property for both classification and regression, the accuracy of these models are comparable to those achieved using the individual descriptors. These functional forms of the descriptors also comply with the physical intuitions regarding the structural modes and displacements of cations governing the ordering at A-site. Interestingly by analyzing the results of Model VII constructed using only key structural modes, it is possible to find a suitable combination of such comprising $Q_{AFE\text{A}}$, $Q_{AFE\text{B}}$, $Q_{AFE\text{C}}$ to predict $E_{\text{diff}}$. However, when descriptors and functionalized forms of those are considered from a pool of geometry-driven and structural modes such as in Model VI, the decision is ruled by the former set. We have further investigated such connections between the features with respect to each other and the target in the later section describing causal structure-property relationships.

**Causal networks:** Exploring feature importances using RF models already show correlative relationships existing between specific features and the property of interest. However, such observations are not enough to understand how the features may be driven by each other; such that it leads to exhibition of particular ordering. We have constructed direct non-Gaussian acyclic structural equation models (LiNGAM) [29–31] to study existing cause-effect relationships among the features with respect to different classes of cation ordering. These models estimate causal ordering of the variables by successively subtracting the effect of each feature from the given data in the model. The convergence is assured based on a fixed number of steps equal to the number of the variables in the model. The ordering strengths (positive or negative) are then evaluated using conventional covariance-based methods such as least squares.

For the multi-label classification into C, L or R, we visualize the causal networks (Figure 6) pairwise by considering exhibition of either (a) C or L, (b) L or R/ C or R and finally into (c) formation of clear layered ordering, respectively. The positive and negative causal ordering strengths are quantified by the green and black arrows in the plots. Interestingly, the causal paths found to predict orderings such as L or R and C or R are the same whereas for distinction between exhibition of C or L, different causal relationships are followed. In Figure 6(a), we have shown the causation effect for C or L-type ordering. To predict C or L-type of ordering, $Q_T$ becomes the top feature in the causal network, sequentially driving the other descriptors such as displacements at $A'$ sites and charge disproportionation modes towards the target. During our data distribution analysis as mentioned earlier, $Q_T$ and $Q_{AFE\text{O}}$ modes are present in L ordering but absent in C. Thus the presence (or absence) of $Q_T$ and $Q_{AFE\text{O}}$ should have a direct effect in classifying L or C. We are able to revisit the same findings within the cause-effect analysis. $Q_T$ has a positive causation effect on $Q_{AFE\text{O}}$ and negative causation effect on $Q_{AFE\text{A}}$. Such observations are in fact true and can be explained by crystal symmetry arguments. The $Q_T$, $Q_{AFE\text{O}}$ and $Q_{AFE\text{A}}$ distortions are shown in Figure 3(b), (c) and (f), respectively. $Q_T$, $Q_{AFE\text{A}}$ and $Q_{AFE\text{B}}$ establish trilinear coupling in Landau free energy expansion. Hence, in the absence of $Q_{AFE\text{B}}$, $Q_T$ and $Q_{AFE\text{A}}$ modes will not couple with each other leading to negative causation effect. It is revealed from the analysis of the structural modes in the section, that in case of layered ordering, coupling between $Q_{AFE\text{O}}$ and $Q_T$ are complimentary leading to gain in energy. For layered ordering, $Q_{AFE\text{O}}$ amounts for displacement of planar $O$ atoms towards higher charge state along the pseudo cubic [001] and [001] directions. $Q_T$ mode vectors are also displaced along the same direction and constructive coupling is possible. In case of $Q_R$, the mode vectors are displaced along [110] and [110] directions in a complementary manner and modify the mode vectors of $Q_{AFE\text{O}}$. Thus, even from the symmetry point of view, constructive coupling between $Q_{AFE\text{O}}$ and $Q_T$ is more feasible. Considering Figure 6(b), it is evident that tuning the AFE displacements systematically for cations at $A'$ sites can affect the disproportionation modes. These features are crucial to establish a direct causal path to predict L or R/ C or R types of ordering. Another viable option to predict these types of ordering follow the path of displacements but also considers the effects of $Q_{AFE\text{A}}$ and $Q_T$. Here, we can see that all the $A'$ site displacements have positive causation effects towards $Q_T$. In tilt distortion $Q_T$, the apical $O$ atoms in the AO plane displace towards the $A'$ site to establish a bonding state. Due to the same reason, $A'$ atoms displace towards O site, leading towards positive causation effect.

For the formation of clear layered ordering, the information about the structural modes become less important as compared to the geometry-driven features. Here, the direct relationships between the cation radii, average cation displacements at different A sites determine if formation of clear layered ordering is possible. If the descriptors related to ground-state energies are included
to construct another network, multiple causal links can then be established following routes heavily dependent on these features. This is expected given the information about the energies becomes just enough to directly distinguish between cases that may form clear-layered ordering. In other words, the energy cut-off that is utilized to label this dataset becomes extremely relevant. It is clear from the Figure 6(c), the charge states of \( A/A' \) are the main decisive factors for classifying clear layered ordering. The charge state of \( B'/B \) leading to \( d^5 \) configuration at \( B' \) site are reported to gain energy for layered ordering with respect to the competing phases. In addition, within stable B-site layered ordering, large charge separation between \( A \) and \( A' \) (i.e., \(+1, +3\) \( AA' \) vs. \(+3, +3\) \( AA' \)) is also reported to be crucial for stable layered ordering. Utilizing such relationships, it is also safe to say that by increasing or decreasing the mode amplitudes of \( QT \), \( CD_{2D} \), one can directly tune the exhibition of C or L type of ordering in double perovskite systems. Similarly, using the direct relationships between \( A_{dis}^x \) and \( CD_{2D} \), one can determine if L or R type of orderings can be formed. For clear layered ordering, the charge state of \( B' \) and \( A \) (or \( A' \)) become the governing factors.

### III. CONCLUSIONS

In summary, we have employed a combination of first-principles computations and ML methods to get insights of cation ordering in double perovskites. Exhibition of such ordering is assessed over a compositional space by generating structures belonging to a wide variety of crystal symmetry with transition metal cations of all possible charge states. The findings of the supervised models constructed with RF algorithm are substantiated by introducing probabilistic accuracy metrics as well as causal orderings between the geometry-driven and structural modes features. We note that even though G-type AFM ordering is considered in this study, similar approach as presented in this work can be utilized to learn about cation orderings assuming different magnetic states.

Based on the machine learning (ML) models, the following specific insights can be outlined. (a) Structural modes are the most important features in the context of classifying layered, columnar and rock-salt ordering. (b) In case of clear layered ordering, the charge separation between \( A \) and \( A' \) is the most important feature which in turn depends on the \( B, B' \) charge separation. The \( 3d(B)-5d(B') \) systems with \( A, A' \) in \(+1, +3\) charge states combination show B-site rock-salt and A-site-layered cation-ordered polar \( \text{P}_2 \) phases. (c) The energy difference for clear layered ordering is found to be directly proportional the cube of the charge state of A-cation and inversely proportional to the \( \log(r_A) \) and \( \log(r_B') \). (d) If we only consider the structural modes then the energy difference turns out to be proportional to anti ferroelectric A-site displacement, in-phase rotation and inversely proportional to the square of the tilt distortions. These are crucial information towards rational design of hybrid improper ferroelectrics, as achieved by utilizing a combination of ML, symmetry and DFT calculations which can not otherwise be captured.

The framework proposed in this work allows for a couple of notable advances in the first-principles and ML community. First is its potential to serve as a template to go beyond the traditional correlative nature of ML models to establish causal relationships between the descriptors space and target property within the data originated from simulations. It also attempts to focus on the interpretability, extensibility of the models rather than solely relying on the final predictions.

### IV. METHODS

**DFT computations:** First-principles calculations are carried out using density functional theory (DFT)\[^{[32]}\] with projector augmented wave (PAW) potentials\[^{[33]}\] and within generalized gradient approximation (GGA) with \( U_E \)[\[^{[34]}\], using Vienna ab initio simulation package (VASP)[\[^{[35]}\]]. The exchange-correlation part is approximated by PBEsol functional [\[^{[36, 37]}\]]. Brillouin zone integrations are performed with a \( \Gamma \)-centered \( 6 \times 6 \times 4 \) \( K \)-point mesh following the crystal symmetry. A cutoff energy of 520 eV is set for all of the calculations, and spin polarization is taken in account. All relaxations are carried out until changes in the total energy between relaxation steps are within \( 1 \times 10^{-4} \) eV and atomic forces on each of the atoms are smaller than 0.01 eV/\( \AA \). All calculations rely on a collinear spin approach and a G-type AFM ordering. We use the on-site effective (\( U_E = U-J_H \)) Coulomb interaction parameter for \( 3d \) states of transition metals such as \( V(U_E=2.0 \text{ eV}) \), \( \text{Cr} \) (\( U_E=3.0 \text{ eV} \)), \( \text{Mn} \) (\( U_E=4.0 \text{ eV} \)), \( \text{Fe} \) (\( U_E=4.5 \text{ eV} \)), \( \text{Co} \) (\( U_E=5.0 \text{ eV} \)), \( \text{Ni} \) (\( U_E=6.0 \text{ eV} \)) and \( 5d \) states of transition metals \( W(U_E=0.0 \text{ eV}) \), \( \text{Re} \) (\( U_E=1.0 \text{ eV} \)), \( \text{Os} \) (\( U_E=1.0 \text{ eV} \)), respectively. The AMPLIMODES (symmetry mode analysis)[\[^{[38]}\]] and PSEUDO[\[^{[39]}\]] are used to determine the magnitude of the structural modes.
SISSO: The compressed sensing methodologies utilized by Ghiringhelli et al. [22] give an ideal solution for generation and selection of nonlinear functionalized descriptors. The selection of the most relevant descriptors is obtained by utilizing the least absolute shrinkage and selection operator (LASSO). The LASSO method as part of SISSO selection scheme uses the sparsity of the $l_1$ norm to effectively reduce a descriptor set to the most relevant descriptors ($d_i$) contained in full set ($D$) via selection of the non-zero terms of the $l_1$ regularized linear least squares approximation of the target property ($P$). The utilization of the $l_1$ norm effectively reduces the NP hard linear least squares approximation of the target property $P(d) = dc$, where $c$ is the $\Omega$ dimensional descriptor $d$. The solution to this equation can be determined by minimizing the following expression,

$$\argmin ||P - Dc||^2_2$$

(1)

Recasting this into a solvable convex problem by allowing for sparsity by adding a $l_1$ prior as a regularization term then yields the expression,

$$\argmin ||P - Dc||^2_2 + \lambda||c||_1$$

(2)

Here the non-zero coefficients $c$ can be utilized to determine the importance of the non-zero coefficients. Thus the coefficients with the greatest value $c$ are the most relevant descriptors to predicting the endpoint.

The generation of nonlinear combinations of descriptors ($d_i$) by applying several mathematical operators such as, $1/x$, $\sqrt{x}$, $x^2$, $x^3$, $\log(x)$, $1/\log(x)$, and $\exp(x)$, on each feature allows for the creating a nonlinear mapping between $D$ and $P$ effectively. In addition, the complexity by combining these functionalized descriptors via summation allows to generate a more effective map between $D$ and $P$. We have considered functionalized descriptors utilizing 3 terms for the purpose of this study. Using such combinations of functionalized descriptors, the best combination of non-linear set of functionalized descriptors can be determined. We have employed logistic regression to obtain the equations leading to classification target.

V. DATA AVAILABILITY

All datasets utilized to construct ML models can be openly accessed via Cation-Ordering-ML github repository.

VI. CODE AVAILABILITY

The datasets utilized to construct ML models, Colab notebooks showing example RF models, SISSO implementation, and causal networks can be freely accessed via Cation-Ordering-ML github repository.

VII. AUTHOR CONTRIBUTIONS

A.G. and S.G. conceived the idea of the project and wrote the manuscript. A.G. performed, supervised all ML frameworks used and developed in this project. G.P. performed the DFT computations under the guidance of S.G. D.P.T. implemented the SISSO method together with A.G.

VIII. COMPETING INTERESTS

The authors have no competing interests to declare.

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