Rapid prediction of phonon structure and properties using the atomistic line graph neural network (ALIGNN)

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The phonon density of states (DOS) summarizes the lattice vibrational modes supported by a structure and gives access to rich information about the material's stability, thermodynamic constants, and thermal transport coefficients. Here, we present an atomistic line graph neural network (ALIGNN) model for the prediction of the phonon density of states and the derived thermal and thermodynamic properties. The model is trained on a database of over 14 000 phonon spectra included in the joint automated repository for various integrated simulations: density functional theory (JARVIS-DFT) database. The model predictions are shown to capture the spectral features of the phonon density of states, effectively categorize dynamical stability, and lead to accurate predictions of DOS-derived thermal and thermodynamic properties, including heat-capacity C_V , vibrational entropy S_{vib} , and the isotopic phonon-scattering rate τ_i^{-1} . A comparison of room temperature thermodynamic property predictions when compared to a direct deep-learning prediction of these material properties as well as predictions based on analytic simplifications of the phonon DOS, including the Debye or Born–von Karman models. Finally, the ALIGNN model is used to predict the phonon spectra and properties for about 40 000 additional materials listed in the JARVIS-DFT database, which are validated as far as possible against other open-sourced high-throughput DFT phonon databases.

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I. INTRODUCTION

The vibrational density of states (DOS) is a fundamental material feature, underpinning several properties related to thermodynamic stability and thermal conduction. Measuring the phonon density of states, for example, by inelastic scattering tends to require access to synchrotron x-ray or high-flux neutron sources, making high-throughput evaluations unfeasible [1]. Evaluation of computational phonon density of states via density functional theory (DFT) has become more mainstream via open-sourced software, such as PHONOPY [2] or ALMABTE [3], allowing for the formation of DFT-based phonon density-of-states databases [4,5]. However, as this method requires evaluating the force sets between pairs of atoms, the calculation becomes increasingly expensive for complex unit-cell materials.

For this reason, it is common to use simple analytic approximations of the phonon DOS when predicting thermal properties based on the Debye linear dispersion and Born– von Karman sinusoidal dispersion relations, for example, Refs. [6–9]. However, these models can dramatically fail for materials that are highly anharmonic, have complex unit cells, or show large acoustic-optical band gaps [10,11]. An attractive route to rapid predictions of phonon DOS and vibrational properties, directly from the crystal structure, is through deep learning [12]. In comparison to analytic approximations, the neural network phonon DOS offers a more accurate

distribution of phonon modes including van Hove singularities and acoustic-optical band gaps, and it does not assume isotropy leading to false degeneracies between phonon modes. In our current paper, anharmonic effects to the phonon DOS are not considered as these require expensive training data in the form of higher-order force constants.

Crystal graph neural networks, which encode features about atoms and their bonding environment in a non-Euclidean graph, have recently shown utility in predicting material properties, such as formation energy, band gap, and elastic constants [13-16]. In their basic form, the nodes of a crystal graph represent individual atoms, and the edges represent interatomic bonds. However, the nearest-neighbor connectivity provides an incomplete picture of the local chemical environment, for example, close-packed bonding environments are difficult to distinguish, but incorporating information about bond angle distributions has provided a means to heuristically classify local structures [17]. The atomistic line graph neural network (ALIGNN) was developed recently as an extension of the crystal graph neural network, which explicitly incorporates bond angles by constructing a line graph over the original crystal graph representation. In the line graph, nodes correspond to bonds whereas edges correspond to pairs of bonds and, therefore, encode the bond angle cosine as a feature. By including bond connectivity and bond angle information, the ALIGNN model showed substantial improvements in prediction accuracy for formation energy, the band gap, and the magnetic moment when compared to a crystal graph convolutional neural network (CGCNN) [13], SchNet [18], MEGNet [19], and hand-crafted features, such as classical force field inspired descriptors [14]. The latter of which is not a graph representation but centers on structural descriptors in the form of distribution functions, such as the radial distribution or angular distribution functions. Numerous machine learning models have been developed to directly predict single scalar-valued thermal and thermodynamic properties, such as heat capacity [20-22], vibrational entropy [21,23], and thermal conductivity [24-27]. However, multiple-output prediction as required for predicting the full phonon DOS spectrum, is relatively less developed [28,29]. In computational spectroscopy, deep-learning forward models have been developed to predict a spectrum (e.g., infrared [30], x ray [31,32], photoemission [33]) directly from the crystal structure. However, as noted in Rankine and Penfold [32], these methods are less common than "reverse" mappings, which instead predict a property based on the measured spectrum.

In this paper, we apply the ALIGNN model to predict the phonon density of states as well as derived thermodynamic and thermal properties, including the vibrational entropy, heat capacity, and phonon-isotope scattering rate. Recently, Kong et al. reported the Mat2Spec model for generating electronic and phononic DOS from material structure features [29]. In their work, both the input features (crystal structure) as well as the output features (DOS) are embedded as multivariate Gaussian distributions. The ALIGNN model, however, has been shown to perform well directly on discretized spectral training data when applied to the prediction of electronic DOS with only modest improvements to model performance achieved using autoencoder-decoder segments to create a lowdimensional representation of the output features [34]. The work of Chen et al. [35] demonstrated the feasibility of predicting phonon density of states using a graph neural network trained directly on discretized phonon DOS data. They applied a Euclidean neural network [E(3)NN], which uses a periodic crystal graph representation and convolutional filters made up of learned radial functions and spherical harmonics such that the neural network is equivariant to three-dimensional group operations [35]. We build from these works with the explicit treatment of bond angles, training on the large dataset of DFT phonon density of states hosted on the JARVIS-DFT database [4,5,23] and by characterizing the performance of the neural network on other structural and transport relevant properties of the DOS, including identification of negative phonon modes and prediction of DOS-derived material properties.

The paper first introduces the ALIGNN model and details of the JARVIS-DFT database used for training and validation. Next, the DOS-derived property equations are introduced to emphasize their differences in the weighting of phonon modes. Finally, we discuss the results of the model first in terms of the direct spectral features of the DOS and then in terms of the derived scalar material properties. We find that prediction of the DOS using the ALIGNN model yields excellent results for the temperature-dependent heat capacity and vibrational entropy and well as the phonon-isotope scattering rate.

II. METHODS AND THEORETICAL BACKGROUND

We will begin by introducing the atomistic line graph representation used to encode the crystal structure in the neural network. Next, we will discuss the dataset used to train and validate the phonon DOS predictions. Finally, we will discuss the property models used to compute DOS-derived properties, such as heat capacity, vibrational entropy, and phonon-isotope scattering rates.

A. Atomistic line graph neural networks

The open-sourced ALIGNN framework [14] is used here to encode crystal structure information in graph representations which then interface with a message passing neural network. This neural network framework can update the embeddings of nodes and edges in the graph while retaining graph connectivity and allowing neighboring nodes and edges to exchange information (pass messages) about their state. There are two graph representations used by the ALIGNN model: (1) an atomistic crystal graph in which nodes represent atoms and edges represent bonds, and (2) a line graph built from the crystal graph in which nodes represent bonds and edges represent bond pairs sharing a common atom (see Fig. 1). The crystal graph is represented as $G = (v, \epsilon)$, where v is the set of nodes, and ϵ is the set of edges with a feature set inspired by the CGCNN model [13]. The following eight node features were used to describe individual atoms: electronegativity, covalent radius, group number, block, valence electron count, atomic volume, first ionization energy, and electron affinity [14]. The edge features, being associated with pairs of atoms/nodes (v_i, v_j) , are the interatomic bond distances r_{ij} . The bond distances are encoded as M-dimensional edge feature vectors using a radial basis function (RBF) expansion with support between 0 and 8 Å. We use 80 edge input features (M =80) with 256 hidden features. Therefore, the edge feature set corresponding to the bond distance r_{ij} is represented as $\epsilon_{ij} = \{ \text{RBF}(||r_{ij} - R_m||) \}_{m=1}^{M}$. Here, R_m is the *m*th center in the bond distance RBF support spanning $\mathbf{R} = [R_1, R_2, \dots, R_M]$.

Each edge in the crystal graph then becomes a node in the line graph. The line graph edges, denoted as t_{ijk} , correspond to triplets of atoms, which in the atomistic graph are labeled by nodes v_i , v_j , v_k , and edges ϵ_{ij} , ϵ_{jk} . The line graph edge naturally represents a bond angle cosine spanned by the three atoms: $\theta_{ijk} = \arccos(\frac{\mathbf{r}_{ij}\cdot\mathbf{r}_{jk}}{|\mathbf{r}_{ij}||\mathbf{r}_{jk}|})$ where the bolded notation \mathbf{r}_{ij} signifies the bond vector connecting nodes (v_i, v_j) . As before with the crystal graph edge features, the bond angle cosines are encoded using an RBF expansion such that the line graph edge feature vector is defined as $t_{ijk} = {\text{RBF}(|\theta_{ijk} - T_m|)}_{m=1}^{M}$, where T_m is the *m*th element in an array of bond angle RBF centers of length 40. The ALIGNN model can efficiently update atom and bond features by alternating message passing updates on both the crystal and line graphs. The crystalline materials treated in this paper are represented using a periodic graph construction, expanded out to 20 nearest neighbors [14].

ALIGNN uses edge-gated graph convolution for updating nodes as well as edge features using a propagation function (f) for layer (l) and node (v_i) with associated feature vector (h_i) and neighbor list (N_i) [14],

$$h_{i}^{(l+1)} = f(v_{i}^{l} \{v_{j}^{l}\}_{j \in N_{i}}).$$
(1)



FIG. 1. Schematic of a crystal and line graph encoding of the Mg₂Si crystal structure. For simplicity of the undirected graph representations, these graphs are constructed by setting the maximum nearest-neighbor value to 1. In the crystal graph (b), nodes represent atom sites and include an atomic feature set consisting of attributes, such as the electronegativity (χ), ionization energy (*E*), and volume per atom (V_{0i}). The edges in the crystal graph represent bonds. Physically, the edge features represent bond distances r_{ij} which are encoded in the model using a RBF. The line graph (c) is constructed on top of the previous crystal graph such that the nodes now represent the bonds of the crystal. The edges, therefore, represent pairs of bonds with a common atom or "triplets" featurized by the bond angles, which once again are encoded using a radial basis function.

As mentioned previously, for this paper, we used 80 initial bond RBF features, and 40 initial bond angle RBF features. The atom, bond, and bond angle feature embedding layers produce 64-dimensional inputs to the graph convolution layers. We used six ALIGNN update layers followed by six edge-gated graph convolution (each with a hidden dimension of 256) updates on the bond line graph. Afterwards, the model performs a global average pooling of the final node vectors, which is used as input for fully connected regression layers that produce the final phonon DOS prediction. The ALIGNN model uses sigmoidal linear unit activation layers because they are twice-differentiable [14], however, this results in an output range of $(-0.5, \infty)$. In order to avoid any unphysical negative density-of-states values, we apply a final rectified linear unit (ReLU) layer to the output tensors that replaces any small, negative values with 0, assuring only positive outputs.

Training was performed with a batch size of 64 samples, learning rate of 0.001, mean-squared error loss function, AdamW optimizer, and 600 epochs. Further details about the ALIGNN model architecture and update procedure can be found in the original model reference [14], recent application to electronic structures [34], and in the shared code repository on GitHub [36].

B. Training dataset

The ALIGNN model is trained on a dataset of over 14 000 material-phonon DOS pairs computed at 0 K using DFT, each labeled with a unique JARVIS-DFT and hosted on the JARVIS-DFT public repository.¹ The second-order force constants used to generate phonons were calculated using a finite difference method implemented in the VASP code [38] using the OptB88vdW functional [39], which includes nonlocal Van der Waals interactions. The *k*-point density and plane-wave

energy cutoff were determined through an automated convergence method described in Choudhary and Tavazza [40], and the crystal structure optimization was performed with energy, forces, and stress relaxation [4]. A Brillouin-zone integration was then performed to calculate the phonon DOS using Gaussian smearing interpolation in the PHONOPY package with a smearing width equal to 1/100 of the full phonon frequency range for the given material [2]. Although the compounds in the phonon database are all evaluated to be energetically stable (i.e., negative formation energies evaluated at 0 K), approximately 18% of the compounds in the JARVIS-DFT phonon dataset have over 10% of the integrated DOS in the negative phonon frequency range. These dynamically unstable compounds were included in the training set because predicting the existence of imaginary phonon modes is an important task in the vibrational analysis of a material. Therefore, the predictive range of the phonon deep-learning model should extend to negative frequencies.

The DOS was then discretized into bins of equal frequency width. We used a dataset with a frequency range of (-300 to)1000) cm^{-1} as this is large enough to contain the minimum and maximum frequencies for nearly all of the compounds in the dataset. The bin size is 20 cm^{-1} , which is the bin size of the discretized DFT phonon DOS hosted on the JARVIS-DFT web page. Additionally, the binned DOS is normalized by the maximum intensity such that the values range from 0 to 1, which improves numerical stability and quality of predictions. As stated in the work of Chen et al. on the E(3)NN phonon DOS model, the correctly scaled DOS is easily recovered from the normalized version because of the physical definition requiring that the integrated DOS equal 3N, where N is the number of atoms in the formula unit [8,29]. This equality provides a straightforward route to recover the appropriately scaled DOS spectrum such that comparisons between different phonon DOSs are meaningful.

During training, the dataset was randomly partitioned into an 80%-10%-10% training-validation(during training)test(fully blind) split. The attributes of the training set are highlighted in Fig. 2. Oxygen is by far the most abundant

¹The DFT-computed electronic and phononic DOS hosted on JARVIS-DFT can be accessed using the JARVIS-TOOLS package or directly through the following FIGSHARE location Ref. [37].



FIG. 2. Attributes of the phonon density-of-states training data set comprising 11 384 total materials. Panel (a) shows the enrichment of each element in the training set. Oxygen was removed from the color map because it is highly enriched with 3162 total counts. The histograms in panels (b)–(d) indicate that the training set is enriched with binary and ternary compounds in the cubic or tetragonal crystal system with an average volume per atom of about (10 to 20) $Å^3$.

element in this dataset, which consists mainly of binary and ternary compounds in the cubic and tetragonal structure types. However, all seven crystal systems are represented in the training dataset.

C. Property models

We focus on the evaluation of three thermodynamic and thermal properties based on the phonon density of states $[g(\omega)]$. The first is the harmonic contribution to the heat capacity, a measure of the heat stored by the phonon modes of a material, which tends to be the majority contribution to the overall heat capacity. Within this harmonic approximation, the lattice does not undergo thermal expansion, and so it is natural to define the heat capacity at constant volume [41]. The heat capacity can be determined directly from the phonon density of states where the phonon modes are weighted by their energy and the temperature derivative of the Bose-Einstein distribution [42],

$$C_{\rm V} = \int k_{\rm B} (\hbar\omega/k_{\rm B}T)^2 \frac{\exp(\hbar\omega/k_{\rm B}T)}{[\exp(\hbar\omega/k_{\rm B}T) - 1]^2} g(\omega) d\omega. \quad (2)$$

At high temperatures, when the full vibrational spectrum is excited, the heat capacity will approach a thermodynamic limit of 1 k_B per phonon mode, yielding the Dulong-Petit limit for molar heat capacity of $C_V = 3NR$, where N is the number of atoms per formula unit, and R is the gas constant. The heat capacity begins to saturate at the Dulong-Petit limit near the Debye temperature (T_D), or the temperature at which the highest phonon mode is activated (see Fig. 3). The Debye temperature relates strongly to the stiffness of the material [41]. As a result, we examine two types of heat-capacity datasets: (1) C_V calculated at a constant temperature (i.e., 300 K), and (2) C_V calculated at a fixed fraction of the Debye temperature (i.e., $0.5T_D$). The constant temperature dataset may be useful when comparing materials for a given application. However, the constant fraction of the Debye temperature is useful when assessing the accuracy of the model for a similar weighting of the density of states in the Eq. (2) integrand. Note that by treating the temperature dependence using an analytic expression based on the phonon DOS, we avoid having to train separate neural networks for each desired temperature.



FIG. 3. Comparison of molar heat capacity versus temperature for two materials (TiS₂ and MgSi₂) with the same Dulong-Petit limit but differing Debye temperatures (T_D). As shown, the heat-capacity values approach the Dulong-Petit limit and, therefore, start to converge above the Debye temperature.



FIG. 4. DOS-derived thermodynamic and thermal properties will weigh regions of the phonon spectrum differently as portrayed in these schematics. (a) The heat-capacity weighting is relatively constant with phonon frequency, whereas (b) the vibrational entropy weighs low-frequency phonon modes more heavily. Finally, (c) the isotope-phonon scattering rate is proportional to $\omega^2 g(\omega)$ and, therefore, weighs high-frequency phonons more heavily.

The vibrational entropy S_{vib} is also evaluated here and describes the range of momentum and position coordinates probed by atoms as they vibrate in a material. As temperature increases, more phonons are excited, and atoms vibrate at higher amplitudes, so the vibrational entropy contribution should increase in magnitude. The vibrational entropy is known to have a role in polymorphic phase transitions and can stabilize lower-symmetry structures with longer bond lengths [43,44]. Additionally, vibrational entropy can significantly influence solubility limits and the location of phase boundaries, making it important to quantify [45]. The vibrational entropy can be determined from a different weighting of the density of states, which stems from multiplying the partition functions for the 3N oscillators available in the material. Lower-frequency phonons tend to be weighted more heavily in $S_{\rm vib}$ and, therefore, typically require high-accuracy descriptions (see Fig. 4),²

$$S_{\text{vib}} = \int k_{\text{B}} \{ [n(\omega) + 1] \ln[n(\omega) + 1] - n(\omega) \ln n(\omega) \} g(\omega) d\omega,$$

where $n(\omega) = [\exp(\hbar \omega / k_{\text{B}} T)]^{-1}.$ (3)

Finally, $g(\omega)$ plays an important role in describing elastic phonon-scattering processes as it defines the scattering phase space or the set of states that an incident phonon can scatter into. To exemplify its role in scattering problems, we calculate the phonon-scattering rate due to phonon-isotope interactions (τ_i^{-1}) , using the natural isotopic abundance for the given material [46,47],

$$\tau_{\rm i}^{-1} = \int \frac{\pi}{6} V_{\rm at} \Gamma \omega^2 g(\omega) d\omega. \tag{4}$$

Here, V_{at} is the volume per atom, and Γ is the mass variance introduced to the lattice by isotopes (see Refs. [47,48] for details). As indicated by the factor of ω^2 in Eq. (4), higher-frequency phonons will be more heavily weighted in the scattering rate calculation (see Fig. 4).

III. RESULTS AND DISCUSSIONS

The model predictions are discussed in this section, first in the context of the direct phonon spectrum prediction and then in terms of derived properties, including the temperaturedependent heat-capacity C_V , vibrational entropy S_{vib} , and the phonon-isotope scattering rate τ_i .

A. Model performance

We use the average mean absolute error (MAE) across the binned density of states to evaluate the performance in predicting the direct spectrum. The average MAE is defined as

MAE =
$$\frac{1}{n} \sum_{i=1}^{n} |y_i - \hat{y}_i|,$$
 (5)

where \hat{y}_i is the predicted value of the ith bin, y_i is the target value of the ith bin, and *n* is the total number of bins.

Figure 5 summarizes the MAE distribution and trends in the test set. The samples of the test set are concentrated at lower MAE values with 78% of the samples showing a MAE of less than 0.086 as represented in the histogram in Fig. 5(a). To better interpret the MAE values, we show examples of the DFT versus ALIGNN-predicted spectra from the first eight MAE bins, which comprise 99.4% of the test set. To better convey the model performance, we show additional example spectra in the Supplemental Material Sec. S1 [49] at finer intervals of MAE. Starting around an MAE level of 0.05, the ALIGNN model begins to miss or average over certain peaks in the spectrum, which is an error seen in deep-learning models for computational spectroscopy [30,33]. The model does, however, tend to capture peak placement and the overall frequency range of the material's phonon DOS relatively well.

Interestingly, we find that MAE is inversely correlated with the average atomic volume in the compound, likely due to the fact that a smaller atomic volume tends yield a higher

²In Fig. 4, the example spectrum is that of Al_2O_3 (JARVIS-ID: JVASP-32) and can be obtained using the JARVIS-TOOLS PYTHON package. Note that this example spectrum comes from a phonon DOS dataset with the following specifications: frequency range of (0–1000) cm⁻¹ and bin size of 5 cm⁻¹. These binning parameters differ from that of the spectra in our training dataset.



FIG. 5. Assessment of model performance in terms of the MAE of individual sample DOS spectra. Panel (a) shows the MAE histogram for ALIGNN-predicted phonon DOS in the test set, which highlights the concentration of samples at low MAE. Below, we show example spectra comparing the DFT DOS (black) to the ALIGNN DOS (colored) from the first eight bins, which comprise 99.4% of the test set. Panel (b) indicates that the MAE tends to decrease with increasing volume per atom. Although panel (c) may suggest that the MAE grows with increasing number of elements in the compound, although this trend is confounded by the fact that the test set is highly enriched with binary and ternary compounds. Finally, panel (d) suggests a more complicated relationship with the crystal system where MAE is anticorrelated with both symmetry and abundance in the training set.

maximum frequency in the phonon DOS. As a result, the model needs to predict peaks across a larger frequency range in these compounds. We additionally note that the MAE tends to increase with the number of unique elements in the compound as well as reduced symmetry of the crystal system. Increased complexity of the formula unit will yield more numerous vibrational modes whereas reduced symmetry results in degeneracy breaking, all of which tend to yield a greater number of peaks in the density of states. Therefore, these trends are logical but may additionally reflect biases in the dataset, which is enriched with binary and ternary compounds as well as cubic and tetragonal materials.

In order to compute meaningful DOS-derived properties, we must first filter out dynamically unstable compounds from the dataset or compounds with imaginary or negative frequency phonon modes. Note that because our training data consist entirely of phonon structure computed at 0 K, this classification of dynamical stability is strictly for 0 K and does not apply at any arbitrary temperature. We chose a more tolerant definition of dynamical stability in order to retain as many samples as possible and because imaginary phonon modes are often used to interpret structural or metal-insulator phase transitions [50,51]. If the integrated area below 0 cm⁻¹ composed less than 10% of the total integrated DOS, then the sample was labeled dynamically stable. The confusion matrix (Fig. 6) is used to compare the ALIGNN and DFT phonon

DOS predictions in terms of this dynamical stability criteria. Note, however, that the ALIGNN model was not retrained as a classifier model for this task. The ALIGNN model is being used as a regression model to fit the full phonon DOS, and then the 10% integrated DOS rule is used to classify the spectra. Although it is important to note that the dataset is overwhelmingly composed of dynamically stable compounds, the ALIGNN model classifies dynamical stability with 90% accuracy where the mostly likely prediction error is a false "stable" labeling. The precision of the classification (i.e., percentage of predicted stable compounds which are DFT stable) is 92.4%, whereas the recall (i.e., percentage of DFT stable compounds correctly predicted as stable) is 95.2%.

B. Derived thermal property predictions

We then analyze model performance in terms of DOSderived properties, including the molar heat-capacity C_V [(in J mol⁻¹ K⁻¹)], the molar vibrational entropy S_{vib} [(in J mol⁻¹ K⁻¹)], and the phonon-isotope scattering rate (in gigahertz). The relationship between properties generated from the target (DFT) DOS versus the predicted (ALIGNN model) DOS are depicted as scatter plots in Fig. 7 with scatter points representing samples in the test set. The central dashed line represents the 1:1 correlation whereas the surrounding dotted lines bound the width of the interquartile range for the target



FIG. 6. Both the DFT and the ALIGNN-predicted phonon DOS are classified as dynamically unstable if more than 10% of the integrated DOS is in the negative frequency range. Based on this classification rule, the confusion matrix compares the DFT prediction (true label) to the ALIGNN prediction (predicted label) for all samples in the test set. As depicted, the majority of sample are correctly classified, but the test set contains primarily dynamically stable compounds. Randomly selected example spectra are shown for each category in the confusion matrix to illustrate the types of DOS errors that can lead to misclassification. The DFT spectrum is shown in black whereas the ALIGNN-predicted spectrum is shown in red.

property distribution, as a way to quantify the spread of the samples.

The molar heat capacity at 300 K [Fig. 7(b)] shows a concentration of samples at intervals of *3NR* since several samples have reached the Dulong-Petit limit for phononic heat capacity by room temperature. As this greatly simplifies the distribution of heat capacity, the correlation coefficient R^2 between the target and the predicted C_V values is 0.998 with a mean absolute error to mean absolute deviation ratio (MAE:MAD) of 0.03, indicating a very low error prediction with respect to the spread in the property distribution (see Figs. 8 and 7 for summaries of DOS-derived property error metrics). The MAD is the average distance between each data point (y_i) and the mean (\bar{y}) of the dataset: MAD = $(1/n) \sum_{i=1}^{n} |y_i - \bar{y}_i|$.

To avoid the influence of the Dulong-Petit limit in the model evaluation, we additionally compare C_V values computed at half of the Debye temperature (T_D) for the entire test set. As shown in Fig. 7(b), this dataset is more distributed since no samples have reached their Dulong-Petit limit of 3NR. Even without the simplification imposed by the Dulong-Petit limit, there is only a modest reduction in model performance in the $0.5T_D$ dataset. Figure 7(i) shows the MAE in the C_V prediction varying within 2 J mol⁻¹ K⁻¹ over a wide percentage range of the Debye temperature.

The molar vibrational entropy $S_{\rm vib}$ also shows a robust correlation between target and predicted values ($R^2 = 0.986$), but

larger error to spread ratio (MAE:MAD = 0.1). As discussed in Sec. II, one reason for the greater prediction error may be that the vibrational entropy integration heavily weights low-frequency phonons. In Supplemental Material Sec. S3, we show the DFT versus ALIGNN phonon DOS for three samples with the highest residuals in $S_{\rm vib}$. A common feature of these spectra is a large DOS peak near 0 cm⁻¹, which when improperly predicted yields a significant S_{vib} prediction error. Moreover, unlike the C_V prediction for which the MAE peaks around 25% of the Debye temperature, the MAE for $S_{\rm vib}$ steadily increases with temperature and saturates above the Debye temperature. Lastly, in the phonon-isotope scattering rate calculation (τ_i^{-1}) , compounds with no natural isotopic abundance and, therefore, no phonon-isotope scattering were filtered out. Nonetheless, the property distribution was highly right skewed. Once again, the ALIGNN DOS model performed well yielding an MAE:MAD ratio of 0.11. Notably, in this case, some of the variance between samples stems not from the phonon DOS, but the mass variance factor Γ , which is calculated separately in the analytic expression. The prediction of the properties of interest (C_V, S_{vib} , and τ_i^{-1}) is robust against several of the errors in the direct DOS prediction apparent from visual inspection. The quality of the property prediction remains high because they are computed as the integral of the DOS, weighted by a frequency-dependent prefactor. Therefore, for these derived properties, it is important for the ALIGNN model to place the phonon peaks in the correct frequency range, but these results are robust against many



FIG. 7. Properties derived from the target (DFT) versus the predicted (ALIGNN) phonon DOS. Note that only samples determined to be dynamically stable both by DFT and ALIGNN are included in thermal property assessments. In panels (a)–(d) scatter points represent individual samples in the test set, whereas the center dashed line shows the 1:1 correlation and the dotted lines highlight the width of the interquartile range in the distribution of target values. The heat map values come from a two-dimensional histogram showing the distribution of samples where red regions indicate a large concentration of samples. Panels (a) and (b) both depict the molar heat-capacity C_V at 300 K and 50% of each material's Debye temperature, respectively. At 300 K, heat-capacity values are closely clustered around intervals of 3NR since several samples have reached the Dulong-Petit limit. Since this physical limit greatly simplifies the prediction, we also show that the C_V predictions remain accurate at across intervals of the Debye temperature (RT) molar vibrational entropy S_{vib} and shows a strong trend between predicted and target values with a few instances of underpredictions. Panel (d) depicts the phonon-isotope scattering rate. The natural isotope abundance for each material was used, which was attained from the isotope database in the PHONOPY package [2]. Compounds without any known isotope variation were excluded. Finally, the distribution of Debye temperatures for the samples in the test set is shown in panel (f).

distortions in the shape of the peak. As shown in Fig. 4, the $S_{\rm vib}$ prefactor preferentially weights low-frequency phonons whereas the $\tau_{\rm i}^{-1}$ prefactor weights high-frequency phonons as such, DOS errors in these regimes will more greatly impact the corresponding property. In Supplemental Material Fig. S2

[49], we illustrate the types of DOS prediction errors that lead to large errors for each DOS-derived property.

To summarize our approach, here we apply the ALIGNN deep-learning model to generate the phonon DOS and, subsequently, apply the equations in Sec. II to derive various



FIG. 8. Model performance is compared for three techniques used to compute DOS-derived material properties, showing that the DOSmediated approach emphasized in this paper yields the most accurate prediction. Techniques (a) and (b) differ primarily in the placement of the deep-learning step relative to the DOS integration step used to derive the material properties. In panel (c), we show the results for the best analytic DOS approximation trialed the Debye approximation. Error metrics include the ratio of the mean absolute error to the MAD of the target property distribution (MAE:MAD) as well as the correlation coefficient between target and predicted values (R^2). Both the molar heat capacity and vibrational entropy are calculated here at RT, 300 K.

thermal and thermodynamic properties. We can compare this DOS-mediated approach to a direct prediction of either heat capacity or vibrational entropy using an ALIGNN model trained directly on the property values. To perform this calculation, we compile two training datasets, one comprising DFT heat-capacity values, and the other comprising DFT vibrational entropy values [i.e., C_V or S_{vib} computed from the DFT phonon DOS using Eqs. (2) and (3)]. We then train separate ALIGNN property models using each dataset. In order to replicate the ALIGNN phonon DOS model as closely as possible in these follow-up tests, we use the same trainingvalidation-test split of the JARVIS-IDS in the database, and we use the same configuration settings related to the graph representation of the material (e.g., maximum number of nearest neighbors, node feature set) and the training (e.g., learning rate, optimizer).

A major advantage of using the DOS-mediated approach is that the temperature dependence of the C_V and S_{vib} is embedded in the model. By modeling the full vibrational structure, we provide knowledge of which phonon modes can be excited at a given temperature. In contrast, a direct deep-learning prediction of temperature-dependent C_V and S_{vib} may require either retraining the neural network for each desired temperature or accumulating property training data labeled with temperature that spans the temperature range of interest. Kauwe *et al.* [20] comments on the difficulty of developing empirical models [52,53] or direct machine-learning models for temperature-dependent heat capacity because thermochemical property data as a function of temperature are not easily attained. Additionally, composition-based features cannot adequately capture nuances regarding the active vibrational modes at a given temperature. When comparing room-temperature properties, we find that the DOS-mediated approach yields a significantly lower model prediction error versus the direct deep-learning approach (see Fig. 8). The MAE for the direct ALIGNN prediction is 9.60 and $16.9 \text{ J} \text{ mol}^{-1} \text{ K}^{-1}$ for the RT C_V and S_{vib} , respectively, compared to the DOS-mediated approach values of 1.58 and 7.26 J mol⁻¹ K⁻¹. The especially poor direct ALIGNN prediction of the heat capacity comes from the concentration of samples around discrete C_V values as the ALIGNN model tends to produce a smoother property distribution. These results reaffirm that predicting the phonon structure from the crystal structure using deep learning is preferable to a direct machine-learning prediction of phonon-based properties.

To better understand the performance of the ALIGNN model, we compared these DOS-derived properties to predictions from analytic approximations of the phonon density of states using both the Debye (linear) and the Born-von Karman (sinusoidal) approximations of the ω versus q relation [9]. Although these dispersion approximations have known limitations, they are still frequently applied to rapidly predict heat-capacity or phonon-scattering rates [7,8,54,55]. Example approximations for the phonon dispersions and phonon DOS are depicted in Fig. 9. We confirm that for roomtemperature property predictions, the Debye and Born-von Karman approximations yield much lower model performance. The MAE for the RT molar C_V is 7.90 (Debye) and 10.5 $J \text{ mol}^{-1} \text{ K}^{-1}$ (Born–von Karman), whereas the MAE for the RT molar S_{vib} is 30.0 (Debye) and 43.9 J mol⁻¹ K⁻¹ (Born-von Karman).



FIG. 9. Schematic of the Debye (linear) and Born–von Karman (sinusoidal) approximations of the phonon dispersion is shown in panel (a). Panels (b) and (c) depict the resulting density of states approximation for the example case of Al_2O_3 compared to the DFT density of states.

C. Large-scale prediction on new compounds

We then applied the trained ALIGNN model to 41 000 crystal structures in the JARVIS-DFT database with unknown phonon DOS and vibrational properties (see Fig. 10). In Supplemental Material Sec. S2 [49], we list the ten highest and lowest predicted property values and corresponding compositions for each of the three material properties considered here: specific-heat capacity at 300 K C_V (in J mol⁻¹ K⁻¹), specific vibrational entropy at 300 K S_{vib} (in J mol⁻¹ K⁻¹), and phonon-isotope scattering rate τ_i^{-1} (in gigahertz). The properties showed expected trends: the specific-heat capacity and vibrational entropy mainly showed an inverse correlation with molar mass and bond strength. The compounds with the highest isotope scattering rate were dominated by light elements with large isotopic variation (such as B and Ge). In Fig. 11 we show the ALIGNN-predicted phonon DOS yield-

ing the lowest and highest contributions to the heat capacity, vibrational entropy, and phonon-isotope scattering rate. The heat-capacity and vibrational entropy comparisons were performed on a per oscillator basis through normalizing by 3N to emphasize the influence of the phonon DOS shape on these properties. As a general trend, a shift of phonon modes from high to low frequencies yields higher room-temperature heat capacity and vibrational entropy but lower phonon-isotope scattering rate.

Additionally, about 830 of the predicted compounds overlapped with the entries in the Materials Project (MP) phonon database generated using density functional perturbation theory [5]. We observe a very close correspondence between our ALIGNN-predicted thermal properties and those derived from the MP phonon spectra (see Fig. 10) even though the calculation method for the phonon dataset used in training



FIG. 10. Comparison between the ALIGNN thermal property predictions and those calculated from the Materials Project density functional perturbation theory (DFPT) phonon structure database. We found 830 overlapping compounds and show a close correspondence between the DFPT and the deep-learning results. The R^2 coefficients and MAE to MAD ratio (abbreviated as MAE:D) are shown on the subplots. Note that this relationship holds even though the phonon DOS used for training of the ALIGNN model were generated using a finite-difference rather than a perturbative approach.



FIG. 11. Summary of predicted phonon properties for 41 000 previously unlabeled compounds in the JARVIS-DFT database. Panels (a)–(c) show the distribution of the 300-K gravimetric C_V and S_{vib} as well as τ_i^{-1} . Panels (d)–(f) show the ALIGNN-predicted spectra yielding the lowest C_V , S_{vib} , and τ_i^{-1} contribution. Note that in the case of C_V and S_{vib} , this is the lowest contribution on a "per-oscillator" basis (i.e., comparing C_V and S_{vib} values divided by 3N). Similarly, panels (g)–(i) show the ALIGNN-predicted spectra yielding the highest contribution to the DOS-derived properties.

of the neural network relied on the finite difference method rather than perturbation theory.

IV. CONCLUSION

The atomistic line graph materials representation preserves the connectivity of the crystal structure and explicitly encodes features describing the atoms, bonds, and bond angles. The technique is shown here to give reasonable predictions of the vibrational structure and properties of a material. In particular, the ALIGNN DOS model yields excellent predictions for three thermodynamic and thermal properties studied, the heat capacity, the vibrational entropy, and the phonon-isotope scattering rate. Through a comparison of room-temperature thermodynamic property predictions, we see that the placement of the deep-learning step relative to the physics-based integration step makes a large difference in prediction quality. We find that using the deep-learning ALIGNN model to predict the DOS spectrum is preferable to learning the DOSderived properties directly, yielding both better accuracy and rich information in one deep-learning step since the DOS encodes for numerous material properties and their temperature dependence.

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