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Introduction

Transition metal dichalcogenides are a large and widely studied class of materials that exhibit a plethora of unique electronic, elastic, thermodynamic and topological properties. They are formed by weakly bound MX_2 stacking-ordered layers, where M is a transition metal and X is a chalcogen, either S, Se, or Te. Chemically stable thin layers of TMDs can be easily obtained via graphene-like mechanical exfoliation from bulk high-quality single crystals due to their weak interlayer van der Waals interactions. Especially, the pristine CdI_2 -type structure is a friendly environment for tweaking and fine-tuning the electronic structure through intercalation of other atomic species and complexes in the region between adjacent chalcogen planes. Although CdI_2 -type TMDs have proven to be a fertile soil attracting research efforts worldwide with the promising to pave the road for a wide range of both technological applications and high-standard fundamental research, there is a dearth of novel systematic, comprehensive studies regarding the effects of different intercalated species on their electronic ground state and thermodynamic stability. In this vein, we have explored the stability, structural, electronic, and bonding properties of $ZrTe_2$ intercalated with several transition metals by combining statistical thermodynamic models with first-principles electronic-structure calculations. Therefore, we intend to demonstrate with our preliminary results how the use of the generalized quasichemical theory within cluster expansion method can be used successfully in describing these systems in a robust, efficient way, with particular focus in probing the superconducting ground state.

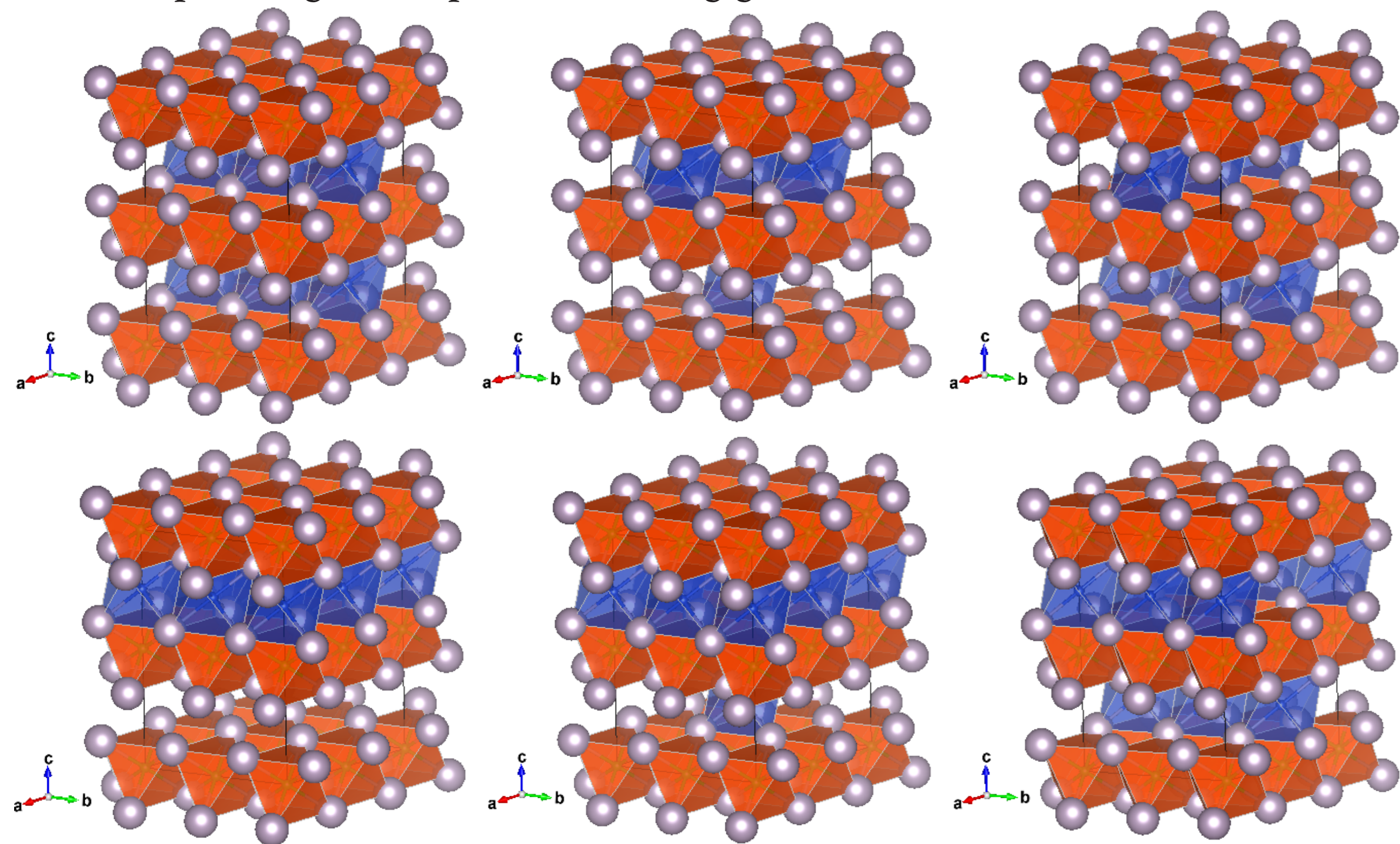


Figure 1: Representation of the $Cu_{0.5}ZrTe_2$ for each class of the $x = 0.5$.

Computational Methods

- Quantum ESPRESSO;
- 70 Ry for wave function energy cutoff and $8 \times 8 \times 4$ k-point mesh;
- Marzari-Vanderbilt smearing with 0.005 Ry gaussian spreading for Brillouin-zone integration;
- PBE, PBE+SOC, rVV10, and vdW-DF2 within projector augmented wave method;
- Convergence threshold: 1.0×10^{-5} a.u. on total energy and 1.0×10^{-3} a.u. on forces for ionic minimization;

Generalized Quasichemical Approximation

In generalized quasichemical approximation (GQCA) the system is described by an ensemble of M individual clusters statistically and energetically independent of the surrounding atomic configuration with n sites that may be occupied by A or B . The clusters are arranged in $(J + 1)$ non-equivalent symmetrically classes with distinct total energies E_j and degeneracies g_j , with $j = 0, 1, \dots, J$.

Within GQCA the mixing free energy per cluster is written as

$$\Delta F = \sum_{j=0}^J x_j \Delta_j + nk_B T [x \ln x + (1-x) \ln(1-x)] + k_B T \sum_{j=0}^J x_j \ln \left(\frac{x_j}{x_j^0} \right)$$

where Δ_j is the reduced excess energies, x is the average B composition in the system, x_j^0 is the j cluster fraction for a given composition x considering an ideal solid solution, and x_j is the cluster fraction probability, *a priori* unknown.

Since the equilibrium state of a many-body condensed system at ambient pressure maintained at constant temperature corresponds to the state of minimum Helmholtz free energy, the cluster probabilities x_j will be those in which ΔF is minimized, that is

$$x_j(x, T) = \frac{g_j \eta^{n_j} e^{-\Delta_j/k_B T}}{\sum_{j=0}^J g_j \eta^{n_j} e^{-\Delta_j/k_B T}},$$

where $\eta = (x e^{\lambda_2/k_B T})/(1-x)$ is obtained solving a n -order polynomial equation. With the set of x_j calculated, an arbitrary property $P(x, T)$ of a given alloy can be estimated as

$$P(x, T) = \sum_{j=0}^J x_j(x, T) p_j,$$

where p_j is the property of each cluster class j .

Structural, electronic, and thermodynamic properties of Cu_xZrTe_2

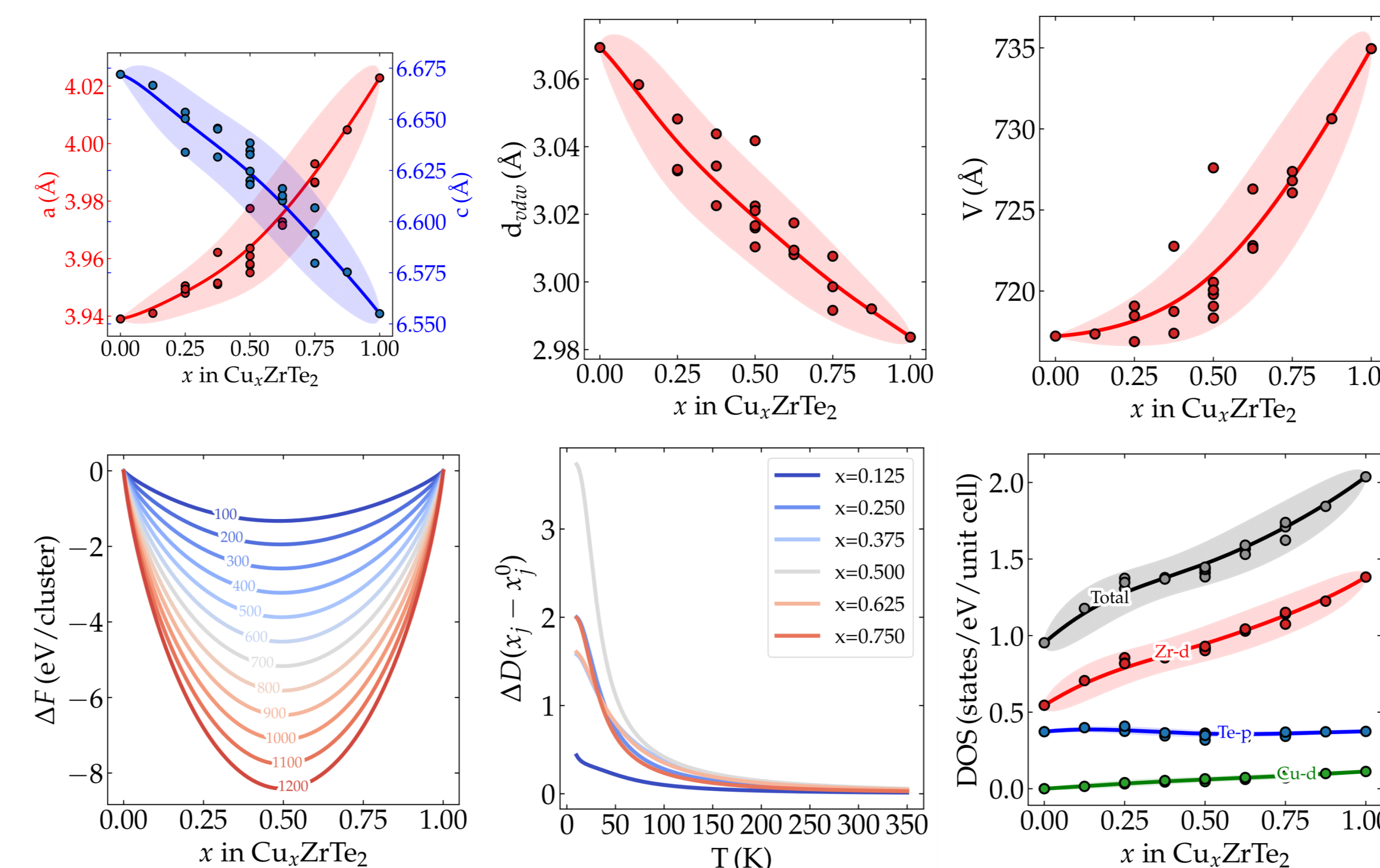


Figure 2: (upper panel) Lattice parameters a and c , van der Waals gap d_{vdw} , volume V , (lower panel) mixing free energy per cluster $\Delta F/M$, Kullback-Leibler divergence ΔD , and density of states at the Fermi level $N(E_F)$ for Cu_xZrTe_2 using the generalized quasichemical approximation. In the present calculations, we've used a $2 \times 2 \times 2$ supercell that results in 22 nonequivalent symmetric clusters with copper atoms situated in octahedral sites between two adjacent chalcogen layers. The calculations shown have been done using opt-vdw-DF2 functional. Colored filled areas represent the possible fluctuations around the mean values, lines are the implemented GQCA model, and points are the fully-optimized ab initio calculations for each cluster. As the mixing free energy assumes negative values along the entire composition range one can say that the copper has the tendency to be homogeneously distributed throughout the entire crystal in $ZrTe_2$ host compound. Along these lines, the Kullback-Leibler divergence, for instance, evaluates the similarity/dissimilarity between the cluster occurrence probability x_j and the probability distribution of cluster j in an ideal solid solution x_j^0 . Above 300 K, therefore, Cu_xZrTe_2 compounds are almost completely disordered, approaching an ideal solid solution indeed. Furthermore, copper intercalation promotes an increase in the $N(E_F)$ favoring electronic correlations such superconductivity and spontaneous symmetry breaking mechanisms as well.

Summary

Using Cu_xZrTe_2 as a test bed we have shown that GQCA model describes the structural, electronic, and thermodynamic properties very well. Despite being a well established thermodynamic approximation, as far as we know GQCA model has not yet been explored to study the effects of different dopants on TMDs. Therefore, we think that our approach can result in unprecedented, and hopefully important contributions in the field. At the present moment we are evaluating the structural properties, COHP functions, density of states and T-x phase diagrams of $ZrTe_2$ intercalated with all the IV-period transition metals in a systematic manner.

In case you have questions or want further information, please don't hesitate to get in touch with us at pedroferreira@usp.br.

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