Vibrational thermodynamics: coupling of chemical order and size effects

Axel van de Walle, Dane Morgan, Eric Wu, Gerbrand Ceder

Abstract— **We study the effects of vibrations in the Pd_3 system using first-principles pseudopotential calculations. We find that upon disordering from the DO_{22} phase, the *decreases* by $0.07k_B$. We explain our results in terms of atomic relaxations and size effects.**

I. Introduction

Materials research and design can be significantly accelerated using first principles computations. As these methods require little or no experimental input, a virtual laboratory can be set up where materials properties are evaluated before they are synthesized. Using a computational approach materials have already been designed for high-energy density rechargeable batteries, for magneto-optical storage and for Hydrogen catalysis. One of the key problems in computational materials science is to determine the structure in which a new composition will form. This is therefore an important part of the research program of Professor Ceder at MIT. In this manuscript we investigate in particular the role that atomic vibrations play in affecting structural stability at finite temperature.

Traditionally, the effects of vibrations have not even been considered in theoretical phase stability studies, which focused primarily on substitutional influences. There is growing evidence, both experimental and theoretical that vibrational thermodynamics can have a significant influence on phase diagrams.

Unfortunately, at present there are only the beginnings of a qualitative understanding of how differences in vibrational thermodynamics arise. In real systems, various mechanisms such as volume differences, bond type differences, internal strain effects, and defect structures (impurities, grain boundaries, etc.) can all contribute to the vibrational thermodynamics, making it difficult to separate out the contributions of each. An advantage of computational approaches is that it is possible to manipulate the system being studied so as to isolate different mechanisms, for example, by removing thermal expansion or restricting internal relaxations. In this work we will use computational approaches to study how relaxations and bonding changes between different chemical orderings influence vibrational entropies.

The key results can be summarized as follows. First-principles pseudopotential calculations for the vibrational entropy of Pd_3V indicate that upon disordering the DO_{22} phase the vibrational entropy *decreases* by $0.07k_B$. This is somewhat surprising since the DO_{22} phase is expected to have stiffer bonds, and therefore a lower vibrational entropy, than the disordered phase. More detailed analysis shows that despite the small size mismatch between Pd and V there is significant relaxation allowed in the disordered phase that is not possible in the DO_{22} structure. The different relaxations occur because any given disordered configuration has much lower symmetry than the DO_{22} phase (although, when the occupations are thermodynamically averaged, the averaged disordered phase has higher symmetry than DO_{22}). It is shown that the greater relaxation allows a stiffening of the Pd-V bonds, which leads to the lowering of the entropy with disordering.

II. Qualitative Framework

First we will discuss a simple qualitative picture of the effects of changing chemical order on the vibrational thermodynamics. We will restrict the discussion to various lattice decorations of a fixed parent lattice at a fixed composition. In the harmonic approximation, the vibrational thermodynamics of a given structure is determined by its dynamical matrix, which in turn is given by the force constant matrix and the masses. At a fixed com-

position and high temperatures the masses contribute a constant term to the vibrational thermodynamics and can therefore be ignored when considering differences. Changes in the vibrational thermodynamics between different lattice decorations must therefore come from changes in the proportions of different force constants, or changes in their actual values.

The sensible starting model of how the force constants are affected by chemical order is what we will call the "bond-proportion model". This model assumes that each type of bond carries with it an approximately fixed force constant, and that changes in the force constants with chemical order are due primarily to changes in the proportions of different types of bonds. This sort of model is often used to give a simple starting Hamiltonian from which more elaborate theoretical calculations are tractable.

If this bond-proportion model is accurate, even qualitatively, there are certain implications for the behavior of vibrational entropies. For example, consider an ordered compound, and compare it to the pure elements from which it is made. As a first approximation the force constants between unlike species are given by the harmonic mean of the force constants between like species. For bonding of this type the bond-proportion model predicts very little change in the vibrational thermodynamics upon disordering. For a strongly ordering material it is to be expected that bonds between unlike species are more stable, and therefore have somewhat stiffer force constants than the harmonic mean of the bonds between like species. The stiffer average force constants would generally cause the ordered phase to have a lower vibrational entropy than the average of the pure elements (which have only like neighbor bonds). Define the vibrational formation entropy of a binary compound $A_{1-c}B_c$ by

$$\Delta S_{form} = S_{ord} - (1-c)S_A - cS_B, \qquad (1)$$

where S_{ord}, S_A, and S_B are the vibrational entropies of the ordered, pure A, and pure B materials, respectively. The above arguments show that the bond-proportion model predicts that for an ordering alloy the vibrational formation entropy would be negative. Another implication of the bond-proportion model is that for an ordering alloy, the disordered phase will have a larger vibrational entropy than an ordered phase of the same composition. This follows from the fact that the disordered phase has fewer unlike neighbor bonds associated with stiff force constants than the ordered phase.

Unfortunately, neither experiments or direct first-principles calculations support the predictions of the bond-proportion model in general. Calculations of the high-temperature limit of ΔS_{form} based on experimentally measured force constants and densities of states show that many ordered compounds have positive values of ΔS_{form} . Furthermore, first-principles calculations on the Cu-Au system found positive values of ΔS_{form} for all the ordered structures studied. These results are not consistent with the bond-proportion model.

Experimental measurements for a number of systems have consistently found that the vibrational entropy increases with disordering, which matches the predictions of the bond-proportion model. On the other hand, first-principles results for Ni_3Al, which is a very strongly ordering compound, show essentially no change in entropy between the ordered and disordered phases.

We propose that to explain, even qualitatively, the changes in vibrational entropy one must go beyond a simple bond-proportion model and incorporate size effects. By size effects is meant the effects on the force constants that are associated with compression and stretching of the bonds. Size effects are not included in the simple bond-proportion model, where all bonds are considered fixed in their strength. For example, if elements A and B have very different sizes, there is no reason to expect A-A bonds to have similar force constants in A and B rich environments, since the A-A bonds will be of very different lengths in the two cases. In the high-temperature limit the relevant thermodynamics can be calculated from the logarithmic average of the density of states ($\langle \ln \omega \rangle$), which is defined by

$$\langle \ln \omega \rangle = \int_0^\infty \ln \omega g(\omega) d\omega. \qquad (2)$$

Here $g(\omega)$ is the vibrational density of states and ω is the frequency. Define the change in $\langle \ln\omega \rangle$ by $\Delta\langle \ln\omega \rangle = \langle \ln\omega \rangle_{disordered} - \langle \ln\omega \rangle_{ordered}$. The change in vibrational free energy (ΔF) and entropy (ΔS) with disordering can then be written simply as

$$\Delta F = k_B T \Delta\langle \ln\omega \rangle \quad (3)$$

$$\Delta S = -k_B \Delta\langle \ln\omega \rangle \quad (4)$$

III. First-principles study of Pd_3V

Pd_3V is a system for which one might expect the bond-proportion model to be accurate. Pd and V have a very small size mismatch $\left(\frac{(V_{Pd}-V_V)}{(V_{Pd}+V_V)/2} = 0.06\right)$ so size effects should not be too large. Pd_3V forms in an ordered DO_{22} structure for temperatures below $1090K$, so it is to be expected that Pd-V bonds will be stronger than the harmonic mean of Pd-Pd and V-V bonds. In addition, Pd and V are on either side of the transition metals in the periodic table. In general, bulk moduli tend to reach a maximum near the middle of the transition metals series. To the extent that a Pd-V bond resembles one between two elements of the middle of the transition metals series, it is to be expected that the Pd-V bonds will be stiffer than Pd-Pd or V-V bonds. Given these arguments, the bond-proportion model predicts that the vibrational entropy should increase upon disordering Pd-V, since fewer Pd-V bonds are present in the disordered phase.

First-principles methods have been used to calculate the vibrational thermodynamics of a few different structures of the Pd_3V system. Calculations have been done with the quasiharmonic method , which extends the harmonic method to approximately include anharmonic terms by allowing volume dependent frequencies. All the entropy values quoted for Pd_3V were calculated in the high-temperature limit at the zero-temperature equilibrium volumes of the structures. The effects of thermal expansion are not reported for simplicity as they are very small, contributing less than $0.01k_B$ to the entropy difference between the DO_{22} and disordered phases at a temperature of $1000K$. The required force constants were fit to ab-initio calculations of forces in supercells with slightly displaced atoms . The calculations are made computationally feasible by restricting displacements to consist of whole planes of atoms, thereby maintaining as much symmetry as possible. Planar force constants are obtained from the displacements and forces according to the relation

$$-\mathbf{F}^{\alpha}(n) = \sum_{m,\beta} \boldsymbol{\lambda}^{\alpha\beta}(n-m)\mathbf{u}^{\beta}(m), \quad (5)$$

where $\mathbf{F}^{\alpha}(n)$ is the force on atom α in layer n, $\mathbf{u}^{\beta}(m)$ is the displacement of atom β in layer m, and $\boldsymbol{\lambda}^{\alpha\beta}(n-m)$ is the $(n-m)th$ layer planar force constant in the direction normal to the planes. The planar force constants can be related to the more usual force constant matrix between atoms α and β by the formula

$$-\boldsymbol{\lambda}^{\alpha\beta}(n) = \sum_{(\mathbf{R}|\hat{\mathbf{e}}\cdot(\mathbf{R}+\boldsymbol{\tau}_{\alpha\beta})=d_n)} \mathbf{D}^{\alpha\beta}(\mathbf{R}), \quad (6)$$

where d_n is the distance between the planes being considered, $\hat{\mathbf{e}}$ is the normal vector to the planes, $\boldsymbol{\tau}_{\alpha\beta}$ is thebasis vector connecting atoms α and *beta* in a unit cell, and $\mathbf{R}$ is a lattice translation vector. $\mathbf{D}^{\alpha\beta}(\mathbf{R})$ is the usual force constant matrix between atoms α and β, separated by basis vector $\boldsymbol{\tau}_{\alpha\beta}$ and lattice vector $\mathbf{R}$, which is calculated by second derivatives of the energy with respect to displacements of those atoms. Eq. (6) shows that the planar force constants are obtained by collecting the usual force constants for all atoms in the appropriate plane, projecting these force constants along the plane normal, and then summing the resulting terms. By performing calculations along a number of directions and applying symmetry relations it is possible to determine all the desired force constants from Eqs. 5 and 6.

Our ab-initio calculations were performed within the local density approximation (LDA) using the VASP package which implements ultrasoft pseudopotentials . To ensure that the errors in the calculated forces did not introduce errors in the vibrational entropies that exceed 0.02 k_B, the following parameters were used. The number of k-points in the first Brillouin zone was chosen to be approximately $(14)^3$ divided by the number of atoms in the unit cell. An high energy cutoff of 365 eV was used to accurately determine the

equilibrium cell shapes, while a cutoff of 211 eV was sufficient for our purposes to obtain accurate forces.

Since we were interested in the change in vibrational thermodynamics upon disordering it was necessary to be able to calculate vibrational properties of the disordered phase. The disordered state was modeled by a Special-Quasirandom-Structure (SQS). The SQS's are small unit cell structures that are constructed to mimic the short-range correlations of a truly random structure as much as possible. They have been shown to give good estimates of disordered values for a number of electronic and vibrational properties. For this study an eight atom SQS (SQS-8) is used, which we believe is large enough to accurately represent the vibrational thermodynamics of the disordered lattice but is small enough to be computationally tractable. A useful way to represent the SQS-8 is in terms of correlations. These are defined as follows. Assign to each lattice site the pseudo-spin value of -1 or +1, depending if the site is occupied by a Pd or V, respectively. Any cluster of sites can then be assigned a cluster function, which is simply the product of the pseudo-spin values on all the sites in the cluster. A correlation is a cluster function averaged over all symmetry equivalent clusters in the parent lattice. Structures with similar correlations tend to have atoms in similar environments. The correlations for the SQS-8 used in this work, as well as the $L1_2$, DO_{22}, and a truly random structure, are given in corr. Note that the correlations for the SQS-8 and random structures are quite similar, showing that the SQS-8 has similar local environments to the disordered phase.

In calculating the force constants some choice must be made about hoi many to include. The entropy (un units of kb) for the DO_{22} structures were -4.47,4.53, and -4.58 for first, second, and third-nearest neighbors. The entropy for the $L1_2$ structures were -4.39, -4.44, -4.48 for first, second, and third-nearest neighbors. Unfortunately, computational limitations restrict us to including only first-neighbor force constants in the SQS-8 structure. The vibrational entropy was -4.54. It can be seen that over the first three neighbor shells the total entropy of the $L1_2$ and DO_{22} structures change by about $0.1k_B$, but that the entropy difference between them is converged to within about $0.02k_B$ by the first-neighbor shell. This suggests that the entropy difference between the SQS-8 and DO_{22} structures is probably also well converged after the first-neighbor force constants. The the entropy of the disordered phase is $0.07k_B$ below that of DO_{22}. The major sources of error in this result are likely to be the use of the SQS-8 to approximate the disordered phase and the limiting of the force constants to the nearest-neighbor shell. The error due to the SQS-8 can be estimated by considering differences between $L1_2$ and DO_{22}. These two structures have an entropy difference of $0.08k_B$ and correlations that are identical for the first-neighbor shell and fairly close after that. For comparison, the SQS-8 and totally random structures also have identical first-neighbor correlations and farther range correlations that are much more similar than those of $L1_2$ and DO_{22}. It is therefore to be expected that the entropy difference between the SQS-8 and random structure would be significantly less than the $0.08k_B$ entropy difference between $L1_2$ and DO_{22}. Based on the correlations for this structure we estimate the error associated with using the SQS-8 at less than $0.04k_B$. The error due to the use of only nearest-neighbor force constants we believe to be about $0.02k_B$, again based on comparison to the entropy difference between the $L1_2$ and DO_{22} structures. Even if we make a very pessimistic error estimate and base the rate of convergence of the absolute vibrational entropies, rather than their differences, we still get an error less than about $0.1k_B$. Even in the presence of these errors, we can still exclude the possibility that the change in entropy upon disordering is large and positive, which is the most important feature of our calculations.

Indeed, the decrease in vibrational entropy upon disordering is in the opposite direction from what would be expected based on the bond-proportion model discussed above. The reason is that size effects, even in this system with almost no apparent size mismatch, contribute significantly to the vibrational thermodynamics. We argued earlier that a Pd-V bond might behave similarly to a bond between two elements of the middle of

the transition metal series, which typically have a larger stiffness. However, elements of the middle of the transition metal series are also characterized by smaller lattice constants. One would then expect Pd-V bonds to be shorter than V-V or Pd-Pd bonds. As we will see, the short Pd-V bond length is indeed at the source of the important relaxations observed in Pd-V. The importance of size effects in this system will be demonstrated by analyzing bond strengths and lengths.

Unfortunately, there is no single parameter which represents the strength of the force constants between two atoms, since this is, in general, a nine element matrix. A great simplification is to represent the force constant matrix in terms of two parameters, a stretching and a bending term. This determination of the stretching and bending terms is done in the following manner. Start by considering a 3x3 force constant matrix between two atoms, represented in a cartesian coordinates with one axis along the bond between the atoms. The diagonal terms of the force constant matrix then represent a stretching and two bending terms, which can be reduced to one by requiring the bending terms to be orientation independent. The remaining off-diagonal terms are assumed to be zero.

The "reduced" force constant matrix is thus fully defined by the elements of its diagonal: an element S (stretching), corresponding to the bond direction and two elements B (bending) corresponding to the other two directions. By a simple rotation, the reduced matrix can then be transformed back into the usual cartesian coordinate system. It will no longer be diagonal, but all the elements will still be given by linear functions of S and B. The values of S and B are then determined by fitting (by a least-squares method) the reduced force constant matrices to the forces obtained from *ab-initio* calculations, as described at the beginning of Sec. III). The values for DO_{22}, $L1_2$, and SQS structures for first nearest-neighbors were -4.48, -4.40, and -4.53 respectively. It is very interesting to note that the entropies calculated with only stretching and bending terms differ by less than $0.01k_B$ from the entropies calculated with the exact nearest-neighbor force constant matrix for all the cases considered.

shiftstiff shows the average stiffness of Pd-Pd and Pd-V first-neighbor bonds as a function of their average distance in both the ordered DO_{22} and $L1_2$ structures and the SQS-8. The stiffness here is taken to be the stretching term defined above. No V-V bond results are included as there are very few of those (none in the ordered phases). This figure shows that in disordering there is a significant change in both the Pd-Pd and Pd-V bond lengths. The change in bond lengths occurs because in the ordered phase all the bonds are constrained by symmetry to be the same length, but in the disordered structure the naturally shorter Pd-V bonds can contract and the naturally longer Pd-Pd bonds can expand. As would be expected, when bonds contract (expand) their stiffness increases (decreases). The contraction of the Pd-V bonds is much greater than the expansion of the Pd-Pd bonds and it is this imbalance which leads to an overall stiffening of the disordered phase and the lowering of the entropy with disorder.

The importance of the relaxations can be seen more quantitatively by removing them in an approximate manner. To do this, we use the stretching and bending model discussed above. We take the stretching and bending parameters for each nearest-neighbor bond in the SQS-8 structure and compute an average for each bond type (Pd-Pd, Pd-V, and V-V). This averaging is needed because a given type of bond (*e.g.*, Pd-Pd) may have slightly different values of S and B, depending on the bond's local environment. These average Pd-Pd, Pd-V, and V-V force constants matrices are an approximation to the "true" force constants we would expect with no symmetry constraints. These force constants are then used to calculate the entropy for both the ordered DO_{22} and SQS-8 structures and the increase in entropy with disordering is found to be $0.26k_B$. This calculation uses a single set of bond length independent force constants for both the ordered and disordered phases and therefore does not include the relaxation differences between the two phases. Without the relaxation effects involved the bond-proportion model applies and the expected entropy increase is seen to occur. Therefore, we

conclude that the relaxations are what cause the bond-proportion model to give an incorrect prediction and the vibrational entropy to decrease with disordering.

It can be shown that the stretching and bending force constants are approximately independent of chemical environment, provided the proper bond length is used. By this it is meant that a given bond, say Pd-Pd, will have similar values for S and B for a given bond length, whether the Pd-Pd bond is in a $L1_2$, DO_{22}, or SQS structure. This raises the possibility of using the values of S and B determined from simple cases to obtain force constants for a variety of complex chemical environments.

This idea is similar to that explored by Sluiter *et al.*, where an attempt was made to develop transferable force constants by averaging over configurations. Sluiter *et al.* found that the averaged force constants were not able to accurately represent the vibrational free energy of different chemical orderings. They attribute at least part of this problem to violation of invariances that the force constants must satisfy. We believe the approach chosen here may be more accurate than the averaged force constants of Sluiter *et al.* for two reasons. Most importantly, the stretching and bending model allows the force constants to depend on bond length, which the work presented in this paper proves to be very important. In addition, by using only the diagonal S and B terms, the force constant matrices automatically satisfy all the invariances associated with crystal symmetry. This should alleviate some of the problems associated with violations of the invariances. Further testing of the stretching and bending model is necessary before its accuracy can be established.

A more detailed discussion of this work on Pd_3V can be found in Phys. Rev. B. 61 5972 (2000).