

First-principles computation of the vibrational entropy of ordered and disordered Pd₃V

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Experimental as well as theoretical work indicates that the relative stability of the ordered and the disordered states of a compound may be significantly affected by their difference in vibrational entropy. The origin of this difference is usually attributed to the fact that disordering reduces the number of stiff bonds between different atomic species in favor of soft bonds between identical atomic species. The results of previous theoretical investigations, however, suggest that this simple mechanism is significantly modified as a result of local atomic relaxations. To gain further insight regarding the importance of relaxations, we employ first-principles calculations to investigate the magnitude of the vibrational entropy difference between the ordered and the disordered state of Pd₃V. Our investigation reveals that bond stiffness changes due to relaxation entirely mask the large configurational dependence of vibrational entropy provided by bond stiffness differences. Our analysis also suggests a simple technique to estimate vibrational entropy based on the relationship between bond length and bond stiffness.

INTRODUCTION

The calculation of phase diagrams from first principles^{1,2} has traditionally been made under the assumption that lattice vibrations have a negligible impact on phase stability. In the last few years, the validity of this assumption has been investigated through numerous experimental³⁻⁹ and theoretical¹⁰⁻²¹ studies.

The effect of the state of order of an alloy on its vibrational entropy is usually attributed to the fact that bonds between different chemical species have a different stiffness than the bonds between identical species. Changing the proportion of the different types of bonds changes the average stiffness of the alloy, resulting in a change of its vibrational entropy. For example, in binary systems with ordering tendencies, bonds between different atomic species are associated with increased stability, which correlates with increased stiffness. Introducing configurational disorder in an ordering system should increase the vibrational entropy, since the process reduces the number of stiff bonds between different species in favor of soft bonds between identical species.¹²

This “bond proportion” mechanism has been thoroughly investigated in model systems (see, for instance, Refs. 22,11,12) and yields the conclusion that the vibrational contribution to the alloy entropy is likely to have a large influence on phase stability. However, the results of more accurate *ab initio* calculations indicate that this simple picture is often unable to explain the observed dependence of vibrational entropy on configuration. In the Cu-Au system,²⁰ for instance, the vibrational entropy of formation of the ordered alloys was found to be positive, contrary to expectation. Equally surprising is the fact that the calculated vibrational entropy change upon disordering the Ni₃Al intermetallic compound¹⁹ was found to be remarkably small, despite the strong ordering tendency of the alloy. Even in semiempirical calculations where an increase in vibrational entropy upon disordering was observed in Ni₃Al,¹⁶⁻¹⁸ the change was attributed mainly to an overall softening of all bonds rather

than to a decrease in the *number* of stiff bonds relative to the number of soft ones.

These findings indicate that the effect of the proportion of different types of bonds is competing with other mechanisms which also influence vibrational entropy. A likely candidate is the effect of relaxations: the stiffness of a bond is a function of its length which, in turn, depends on the local relaxations that take place in the alloy. Relaxations are likely to reduce the magnitude of vibrational entropy differences for the following reason: When bonds of different lengths are forced to coexist in an alloy, each type of bond will be unable to reach its “ideal” length and, on average, short bonds will be forced to elongate while long bonds will be expected to shorten. Since bond stiffness is typically inversely proportional to bond length, the stiff bonds would then be softened and the soft bonds stiffened. Hence, relaxations tend to dampen large changes in vibrational entropy.

This would indicate that large vibrational entropy differences are likely to be found in systems where there is a strong bonding strength difference between like and unlike bonds and where there is little size mismatch between the atomic species, so that the effect of bond stiffness differences is not hindered by the effect of relaxations. The Pd-V system appears an ideal candidate for two reasons. First, the size mismatch between Pd and V is small: Our *ab initio* calculations indicate that the lattice parameters of fcc Pd and of V, artificially constrained to be in an fcc structure as well, differ by only 4%. Second, Pd-V bonds are expected to exhibit a stiffness that exceeds the average stiffness of Pd-Pd and V-V bonds. The latter can be deduced from the characteristic trend of the bulk modulus of transition metals across the periodic table: Early transition metals are soft because their bonding orbitals are only partially filled. Stiffness reaches a maximum when the bonding orbitals are full and then decreases as the antibonding orbitals fill up. Pd and V are at each end of the transition metal section of the periodic table and are thus rather soft. When they are alloyed, the average number of valence electrons per atom is such that the bonding orbitals are closer to their optimal filling, suggesting that

the stiffness of a Pd-V bond should be larger than the *average* stiffness of Pd-Pd and V-V bonds. (Note that since pure Pd is significantly stiffer than pure V, a Pd-V bond can still be softer than a Pd-Pd bond.)

Our investigation reveals that, even in this apparently relaxation-free system, the large configurational dependence of vibrational entropy provided by bond stiffness differences between different type of bonds is entirely masked by relaxation effects which change the stiffness of a given type of bond. The inability to entirely decouple the effect of bond stiffness from the effect of bond length leads to the rather surprising behavior of the vibrational entropy in the Pd-V system.

In the remainder of this paper, we will first describe the methodology used to calculate vibrational entropy in the Pd₃V compound in both its ordered and disordered state. We will then present the results of these calculations, describing the physical origin of this system's unexpected lattice dynamics. The mechanism we identify is unlikely to be limited to the Pd-V system and points to an important effect that needs to be accounted for in order to properly model the configurational dependence of vibrational entropy.

I. METHODOLOGY

In the harmonic approximation, the vibrational entropy of a structure can be obtained from the phonon density of states²³ $g(\nu)$. Above the Debye temperature of the solid, the high temperature limit is quickly reached and this dependence reduces to

$$S_{\text{vib}} = -3k_B [1 + \ln(k_B T)] - k_B \int_0^\infty \ln(\nu) g(\nu) d\nu.$$

Since the first term is structure-independent, it has no effect on phase stability and will be ignored in the following analysis. The high-temperature limit is a good indicator of how large the effect of vibrations is likely to be in a given system, as vibrational entropy reaches its maximum in the high temperature limit.

The harmonic approximation can be made more realistic by allowing the phonon frequencies to be volume dependent. This approach, called the quasiharmonic approximation,²³ enables the calculation of thermal expansion as well as its impact on the vibrational entropy. Once the volume-dependence of energy $E(V)$ and vibrational entropy $S_{\text{vib}}(V)$ is known, the equilibrium volume at temperature T is found by minimizing the free energy $F = E(V) - TS_{\text{vib}}(V)$ with respect to V . This technique has been used in previous computational investigations of the vibrational entropy.^{17,19,20}

The phonon density of states of an ordered compound can be accurately calculated through a variety of first-principles methods. Either the linear response technique^{24,25} or the fitting of a Born-von Kármán spring model to forces obtained from *ab initio* calculations^{10,26} can be used. In contrast, the case of a disordered alloy presents numerous difficulties associated with large computational requirements. The most direct way to model the disordered state is to rely on a large supercell calculation where the occupation of the lattice sites is randomly chosen. Unfortunately, both the linear response and the spring constant fitting approaches become impractical for very large supercells.

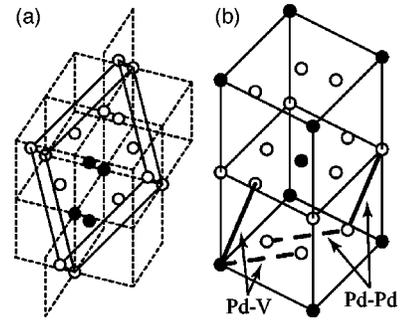


FIG. 1. (a) Eight-atom SQS used to model the disordered state. (Primitive unit cell shown.) (b) Constraints on bond lengths originating from the symmetry of the ordered DO_{22} structure. (Conventional cell shown.) Bonds represented by identical line styles have identical lengths.

A computationally efficient way to model the disordered state is to rely on a so-called special quasirandom structure²⁷ (SQS). A SQS is the periodic structure that best approximates the disordered state in a unit cell of a given size. The SQS approach has been used very successfully to obtain electronic and thermodynamic properties of disordered materials (see, for example, Ref. 28). More recently, a SQS has been applied to the *ab initio* calculation of vibrational entropy in disordered alloys.¹⁹ The accuracy of the SQS approach has also been benchmarked using embedded atoms potentials which allow the computation of the vibrational entropy of a large supercell simulating the disordered state.²⁹ A SQS having only 8 atoms in its unit cell was found to already provide a good approximation of the disordered state.

The quality of a SQS is described by the range within which the statistical correlations between the occupation of different lattice sites mimics the ones of the disordered state. These correlations are defined as follows: Spinlike variables are assigned to each site of the lattice (-1 for Pd and $+1$ for V). The correlation associated with a given cluster of sites (e.g., a pair of neighboring sites) is then obtained by taking the product of the spins of each site of this cluster and by averaging this quantity over all clusters which are equivalent by the symmetry of the parent lattice. For an fcc lattice at concentration $3/4$, the eight-atom SQS shown in Fig. 1(a) is able to reproduce the nearest-neighbor pair correlation of the disordered state exactly. Other longer range and multi-body statistical correlations are approximately reproduced, as shown in Table I. To estimate the magnitude of the errors introduced by the approximation of these other correlations, we have computed the vibrational entropy of the $L1_2$ structure which has the same nearest-neighbor correlation as the equilibrium DO_{22} ordered structure, but different longer range and multi-body correlations. The vibrational entropy of the $L1_2$ and the DO_{22} structures differ by $0.08k_B$, but the difference between the eight-atom SQS and the true disordered state is expected to be only half as much, since their longer range and multibody correlations are more similar, as shown in Table I.

The large computational requirements of the linear response technique limits its use to very symmetric small-cell structures. We therefore rely instead on the fitting of spring constants to *ab initio* calculations of the forces acting on the

TABLE I. Correlations of the structures used. p_n denotes the n th nearest neighbor correlation while t_{lmn} denotes a triplet made of overlapping p_l , p_m , and p_n pairs.

| Structure | p_1 | p_2 | t_{111} | t_{112} | t_{113} | t_{114} |
|-----------|-------|-------|-----------|-----------|-----------|-----------|
| $L1_2$ | 0 | 1 | 1/2 | -1/2 | 1/2 | -1/2 |
| DO_{22} | 0 | 2/3 | 1/2 | -1/6 | 1/6 | 1/6 |
| SQS-8 | 1/4 | 1/3 | -1/4 | 0 | -1/12 | -1/6 |
| Random | 1/4 | 1/4 | -1/8 | -1/8 | -1/8 | -1/8 |

atoms when they are perturbed away from their equilibrium positions. Our *ab initio* calculations are performed within the local density approximation (LDA) using the VASP (Refs. 30,31) package which implements ultrasoft³² pseudopotentials.³³ To ensure that the errors in the calculated forces do 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 is chosen to be approximately $(14)^3$ divided by the number of atoms in the unit cell. A high energy cutoff of 365 eV is used to accurately determine the equilibrium cell shapes, while a cutoff of 211 eV is sufficient for our purposes to obtain accurate forces.

The precision of the spring constant fitting technique can be controlled by gradually including longer-ranged spring interactions until the value of vibrational entropy converges. While the absolute value of the vibrational entropy converges slowly with respect to the range of interaction in the Pd-V system, vibrational entropy differences converge more rapidly. As shown in Table II, the vibrational entropy difference between the $L1_2$ and the DO_{22} structures is essentially independent of the range of interactions included. A nearest-neighbor model appears able to model vibrational entropy differences with a precision of about $0.02k_B$, whereas typical vibrational entropy differences are of the order of $0.1k_B$. We exploit this fact to describe the disordered state, where longer ranged interactions would be prohibitive to calculate, using nearest-neighbor spring constants only. Note that due to the low symmetry of the SQS, a nearest-neighbor model still involves the evaluation of 50 distinct parameters in the spring tensors.

The use of such a short range of interactions is not unusual: It has been observed¹⁰ that even though a long-range spring model is required to model all the features of the

TABLE II. Vibrational entropy (in k_B) as a function of the interaction range included in the spring model. Range is expressed as the number of nearest neighbor shells. Only stretching and bending terms are included for the column labeled 1(sb) while the column 1(len) presents the results of a model where bond stiffness is allowed to depend on bond length only (see text).

| Structure | 1(len) | 1(sb) | 1 | 2 | 3 |
|-------------------|--------|-------|-------|-------|-------|
| $L1_2$ | -4.39 | -4.40 | -4.39 | -4.44 | -4.48 |
| DO_{22} | -4.42 | -4.48 | -4.47 | -4.53 | -4.58 |
| SQS-8 | -4.56 | -4.53 | -4.54 | | |
| $L1_2 - DO_{22}$ | 0.03 | 0.08 | 0.08 | 0.08 | 0.10 |
| $SQS-8 - DO_{22}$ | -0.14 | -0.05 | -0.07 | | |

TABLE III. Calculated properties of the ordered (DO_{22}) and the disordered state (approximated by an 8 atom SQS). Bulk modulus and volume are given at 0 K while the other quantities are the high-temperature limiting values.

| Quantity | Units | DO_{22} | SQS-8 |
|-------------------------------------|---------------------------------|-----------|--------|
| Bulk modulus | GPa | 215 | 191 |
| Atomic volume | $\text{\AA}^3/\text{atom}$ | 13.808 | 13.891 |
| Average Grüneisen parameter | | 2.41 | 2.24 |
| Linear thermal expansion coef. | 10^{-6} K^{-1} | 11.2 | 11.6 |
| Temperature dependence of S_{vib} | $10^{-6} k_B / (\text{K atom})$ | 243 | 234 |

phonon DOS, an integrated quantity such as the vibrational entropy converges much faster with respect to the range of interaction included. It is important to note that once convergence with respect to interaction range is reached, this approach should be just as reliable as the linear response method, since both methods rely on the same assumption of harmonicity. The fact that short-range interactions are sufficient to reach a high accuracy favors the use of a Born-von Kármán model and enables the evaluation of the vibrational entropy of an eight-atom SQS at a reasonable computational cost.

It is possible that this rapid convergence of vibrational entropy differences is fortuitous and unique to the $L1_2$ and DO_{22} structures. In this case, the speed of convergence of the absolute vibrational entropies, rather than their differences, should be used as a measure of precision. Although this pessimistic estimate is of the order of $0.1k_B$, our results will remain conclusive in the presence of an error of this magnitude.

II. RESULTS

Our main result is that the calculated vibrational entropy of the disordered state is $0.07k_B$ lower than the one of the ordered state (DO_{22} structure), contrary to expectation (see Table II). Using even the most pessimistic estimate of the precision of our approach ($0.1k_B$), the vibrational entropy change upon disordering is no larger than $0.03k_B$, which is small compared to typical vibrational entropy changes, which are of the order of $0.1k_B$. A relaxation-free ordering system with a strong ordering tendency would be expected to yield among the largest vibrational entropy increase upon disordering.

A quasiharmonic treatment enables the evaluation of the temperature dependence of this entropy difference. While the temperature dependence of the vibrational entropy is large in both the ordered and the disordered state (see Table III), they are almost identical and have little impact on phase stability. This identity is remarkable: the ordered and disordered materials have a different bulk modulus and a different Grüneisen parameter (see Table III), but these two differences offset one another. Interestingly, the same cancellation was observed in our investigation of the order-disorder transition of Ni_3Al .¹⁹ In the discussion which follows, we can thus use the vibrational entropy change calculated in the high-temperature limit at the equilibrium lattice constant at 0 K as a reliable approximation of the vibrational entropy change at any temperature above the Debye temperature.

Another unexpected finding is that the bulk modulus of the disordered state is smaller than that of the ordered state, which is in apparent contradiction with our claim that the disordered state is “stiffer” than the ordered state. However, one must keep in mind that vibrational entropy depends on the average stiffness of *all* possible vibrational modes, while bulk modulus measures the stiffness of only one mode. The Pd-V system thus provides an example where estimates of the vibrational entropy based on bulk modulus, such as the Debye-Grüneisen model,³⁴ can be misleading.

III. DISCUSSION

The fact that the vibrational entropy change upon disordering does not have the sign that one would expect for an ordering system merits further analysis. This section demonstrates that the origin of this surprising result can be traced back to the effect of local relaxations. We first present a simple model that allows us to isolate the origin of the vibrational entropy differences in this system. We then introduce a precise mechanism that is able to explain our results before proceeding to show that this particular mechanism is indeed at work in Pd₃V.

Consider a simplified spring model obtained by including only stretching and bending terms in the first nearest-neighbor spring tensors. These terms can be read from the diagonal elements of the spring tensor associated with a given pair of atoms, when this tensor is represented in a Cartesian basis with one axis aligned along the segment joining the two atoms in question. In addition, the bending terms are constrained to be orientation independent. The resulting tensor contains only two independent spring constants, a stretching term s and a bending term b :

$$\begin{pmatrix} -s & 0 & 0 \\ 0 & -b & 0 \\ 0 & 0 & -b \end{pmatrix}.$$

The error introduced by this approximation (relative to using the full first nearest-neighbor tensor) never exceeds $0.01k_B$ for all fcc structures tested [see Table II, columns 1(sb) and 1]. In these calculations, the simplified spring model is applied to the fully relaxed geometries, as determined from *ab initio* calculations. Note that keeping only stretching terms would be an oversimplification, as it can result in errors comparable in magnitude to the typical values of the vibrational entropy of formation ($\pm 0.2k_B$). These errors are nonsystematic and do not cancel out when taking entropy differences.

This simple spring model is useful from a conceptual point of view, as it lets us compare the stiffness a given type of bonds (e.g., Pd-Pd, V-V, or Pd-V) in different structures: the spring tensors have the same form regardless of the symmetry of the bonds’ environment. Figure 2 shows the values of the stretching (s) and bending (b) terms of the spring tensor of bonds of various lengths taken from a set of fcc-based structures ($L1_2, DO_{22}, SQS-8$, fcc Pd, and fcc V, each taken at two different volumes). Bond stiffness correlates reasonably well with bond length, as seen by the least squares fit shown in Fig. 2. Bond stiffness typically decreases with bond length. The fact that the same relationship between bond stiffness and length holds throughout different

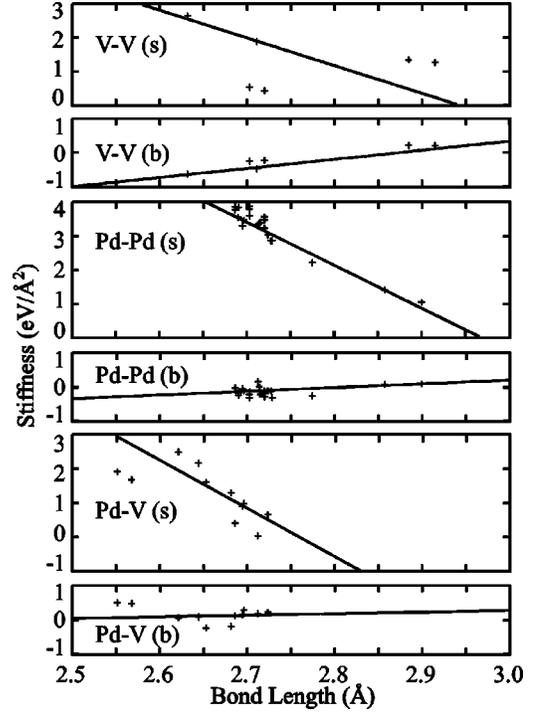


FIG. 2. Stretching (s) and bending (b) terms of the nearest-neighbor spring tensor as a function of bond length. Each point corresponds to one type of bond in one of a set of fcc structures ($L1_2$, DO_{22} , $SQS-8$, fcc Pd, and fcc V, each taken at two different volumes).

structures is an important feature that will lead us to a simple mechanism explaining our results for the Pd-V system. While both the stretching and bending terms are important to consider for quantitative purposes, the magnitude of the stretching term only provides a convenient measure of a bond’s stiffness for the purpose of the following qualitative discussion.

We argued earlier that a Pd-V bond resembles 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 the average length of V-V and Pd-Pd bonds. As shown in Table IV, the average bond length and stiffness in the disordered state are in perfect agreement with this picture. Note that, while Pd-V bonds are stiffer than the *average* stiffness of Pd-Pd and V-V bonds, as expected, Pd-V bonds are nevertheless softer than Pd-Pd bonds.

TABLE IV. Average bond length and bond stiffness (along the stretching direction) in the disordered state. The row labeled “average” reports the arithmetic average of the length of Pd-Pd and V-V bonds and the geometric average of their stiffness.

| Bond | Length (Å) | Stiffness (eV/Å ²) |
|---------|------------|--------------------------------|
| Pd-Pd | 2.743 | 3.06 |
| V-V | 2.763 | 0.69 |
| Average | 2.753 | 1.45 |
| Pd-V | 2.628 | 2.21 |

TABLE V. Average bond length and bond stiffness (along the stretching direction) in the ordered state.

| Bond | Length (\AA) | Stiffness (eV/\AA^2) |
|-------|-------------------------|---------------------------------|
| V-Pd | 2.693 | 0.61 |
| Pd-Pd | 2.693 | 3.44 |

The situation is quite different in the ordered state: the high symmetry of the structure constrains the Pd-V bonds to have the same length as the Pd-Pd bonds [see Fig. 1(b)]. The average bond length tends to be much closer to the Pd-Pd “ideal” length than to the Pd-V “ideal” length because Pd-Pd bonds are stiffer than Pd-V bonds. The result is an ordered alloy where Pd-V bonds are significantly longer than they would be in the absence of symmetry constraints while the Pd-Pd bond lengths are only slightly affected. Pd-V bonds are therefore unusually soft in the ordered state, while the stiffness of Pd-Pd bonds is nearly unaffected. This tends to make the ordered state softer and is responsible for its higher vibrational entropy. The average bond length and stiffness in the ordered state shown in Table V support this interpretation.

The fact that disordering shortens the Pd-V bond while leaving the Pd-Pd bonds mostly unchanged on average can be seen from the histogram of the bond length distribution (Fig. 3). The impact of these bond length changes on stiffness is best illustrated by plotting the change in average bond length and stiffness upon disordering, as illustrated in Fig. 4. The dramatic stiffening of the Pd-V bonds and the slight softening of the Pd-Pd bonds in the disordered state, relative to the ordered state, is clearly visible.

Static displacements of this magnitude should be visible in diffuse scattering measurements. Such measurements have been performed in Pd_3V (Ref. 35) and in a related system, Pt_3V (Ref. 36). One of the authors of Ref. 35 (Ducastelle) has indicated to us that the more precise measurements made on Pt_3V should give us a reliable upper bound on the magnitude of the static displacements in disordered Pd_3V , where the determination of the static displacements was less precise. We will thus compare our results with the Pt_3V measurements only.

As the scattering factor of V is much smaller than the one of Pt, it is difficult to measure shifts in the Pt-V and V-V bond lengths. Unfortunately, these are precisely the bonds we predict to be the most affected by disordering. The experimental nearest neighbor average Pt-Pt bond length shift

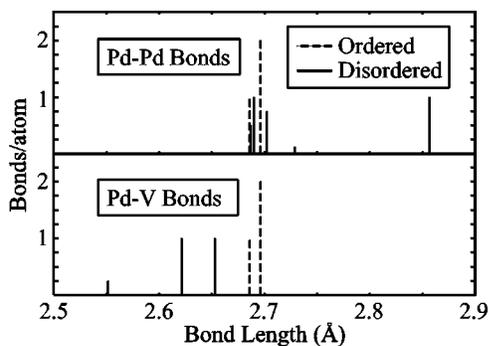


FIG. 3. Bond length distribution.

is reported to be 0.3% of the lattice parameter, which is somewhat smaller than ours (1.2% of the lattice parameter). This discrepancy can be easily explained by the fact that we model disordered Pd_3V as a perfectly disordered material, while disordered Pd_3V actually exhibits short-range order. Fully disordered Pd_3V is naturally expected to exhibit larger relaxations. Note that the presence of short-range order does not invalidate our discussion. In the presence of short-range order, both the traditional “bond proportion” mechanism and the effect of relaxations will decrease in importance, but they would still give rise to competing and comparable contributions to the vibrational entropy change, which is our main observation. As such, existing experimental observations do not contradict our findings. Unfortunately, the most salient feature of our predicted static displacements, the shortening of Pd-V bonds, has not yet been confirmed experimentally.

Perhaps the easiest way to separate the effect of the “bond proportion” mechanism from the effect of relaxations is to construct a model system where bonds always have the opportunity to reach their “ideal” length, regardless of the symmetry of their local environment. The average stretching and bending force constants obtained in the disordered state, listed in Table IV, are used as an approximation to the “true” force constants that would be expected in the absence of symmetry constraints. These force constants are used to calculate the vibrational entropy for both the ordered DO_{22} and SQS -8 structures. The vibrational entropy change upon disordering then becomes $0.26k_B$, which is large and positive, as expected when the “bond proportion” mechanism operates alone. The large configurational dependence of vibrational entropy provided by the “bond proportion” mechanism is thus entirely masked by relaxation effects to yield vibrational entropy difference of $-0.07k_B$.

While the above model system is useful for illustrative purposes, we have to verify that the difference between $0.26k_B$ and $-0.07k_B$ can really entirely be attributed to the effect of relaxations. For instance, this difference includes the error introduced by replacing each bond’s force constants by average force constants. Vibrational entropy is not a linear function of the force constants, and averaging the latter could bias the former. Moreover, bond stiffness could vary for reasons other than bond length change: for example, the local charge density in the neighborhood of a given bond could vary. For these reasons, we now introduce a model

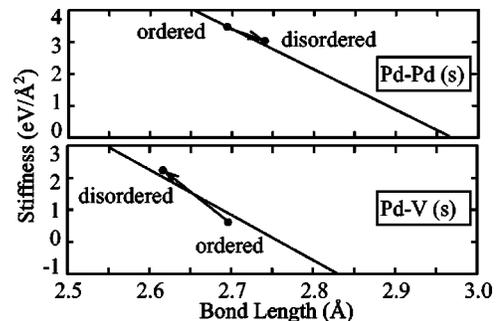


FIG. 4. Shift in average bond stiffness (along the stretching direction) and bond length upon disordering. The fitted line of Fig. 2 is shown for reference.

system which (1) does not rely on averaged force constants and (2) only accounts for bond stiffness change due to bond length changes.

To show that the effect of relaxations alone can explain our results, we replace the true stiffness of each bond by the one predicted from bond length through a simple least squares fit (shown in Fig. 2). While this simplified model exhibits a limited accuracy [see column 1(len) of Table II], it is clearly able to predict that the vibrational entropy of the disordered state is lower than the one of the ordered state. In the simplified model, a bond's stiffness is uniquely determined by its type (Pd-Pd, Pd-V, or V-V) and its length. Variations in bond stiffness that are not due to bond length are ignored, leaving only relaxations as the possible source of the higher stiffness of the disordered state.

It is worth noting that our suggestion of defining bond characteristics that are transferable (i.e., applicable to different structures) bears some resemblance to an earlier attempt to define transferable "configuration averaged force constants" (CA FC).³⁷ However, our approach differs in three important respects. First, we keep only stretching and bending terms in the spring tensors, thus avoiding the incompatibilities in the form of the spring tensor when the symmetry environment of a bond differs in distinct structures. Second, we do not try to define a universal bond-specific stiffness but instead define a universal stiffness versus length relationship. The stiffness of a bond is thus allowed to vary in different structures when its length varies. Finally, we do not attempt to define force constants that also predict the correct equilibrium geometry of a structure. In a typical *ab initio* phase diagram calculation, the exact equilibrium geometry is already known, as it is a by-product of the calculation of the energy of a given structure.

IV. CONCLUSION

The ordering tendency of the Pd-V system would indicate that Pd-V bonds should be stiff relative to Pd-Pd and V-V bonds. Based on this observation, one would expect the vibrational entropy change upon disordering to be large and positive. Instead, our calculations indicate a negative vibrational entropy change. The origin of this surprising result lies in the fact that the Pd-V bonds are stiffer only when they are allowed to relax to their short "ideal" length, which can happen in the disordered state but not in the ordered state, due to symmetry constraints. The stiffening of the Pd-V bonds in the disordered state more than compensates for the fact that there are less Pd-V bonds in the disordered state. The larger stiffness of the disordered state translates into a vibrational entropy that is lower than the one of the ordered state. We prove that this mechanism indeed determines the observed sign of the vibrational entropy change upon disordering through two model systems. In one system, we entirely remove the effect of relaxations and find that the vibrational entropy change now has the positive sign typically expected in a ordering system. In a second model system, we only include bond stiffness changes that can be associated with bond length changes and find that the vibrational en-

ropy decreases upon disordering, in agreement with the results of our more accurate calculations. These two results unambiguously show that relaxations play an essential role in determining vibrational entropy changes in the Pd-V system.

Bond stiffness and bond length are strongly correlated and predictions regarding the magnitude of vibrational effects in a given system must take this into account, even in a system characterized by small size mismatch. In the Pd-V system, accurately modeling local relaxations appears more important than taking into account long-range interactions in the Born-von Kármán spring model, a feature that we observed in our previous investigation of the Ni-Al system¹⁹ as well.

Bending and stretching terms of the nearest-neighbor spring tensors already provide accurate vibrational entropy differences in the Pd-V system. Interestingly, using the same simplified models to fit the results of our previous calculations on the Ni-Al system,¹⁹ achieves a comparable precision. If further investigations indicate that many systems share this characteristic, this will open the way for a computationally inexpensive method to estimate vibrational entropies. Indeed, for low symmetry structures, most of the computational burden arises from the evaluation of the numerous off-diagonal elements of the spring tensors. The importance of relaxation also suggests that efforts to obtain a more precise description of the configurational dependence of vibrational entropy for the purpose of calculating phase diagrams should be aimed at including more terms in the cluster expansion³⁸ of vibrational entropy rather than using longer ranged spring models.

Our results also suggest a way to construct "transferable" force constants that would enable the calculation of the vibrational entropy of a large number of structures without having to recalculate force constants from *ab initio* calculations for each of them. Our results show that, while the stiffness of a bond is unlikely to be transferable, the relationship between stiffness and length for a given type of chemical bond *is* transferable. Such transferable relationship can easily be determined by a fit to the force constants calculated from first-principles in a small set of structures. The vibrational entropy of any other structure could then be determined solely from the knowledge of its equilibrium geometry, an information that is already a by-product of any *ab initio* phase diagram calculation. This approach captures the essential physics determining vibrational entropy differences in alloys and presents an extremely promising way to include vibrational effects in phase diagram calculations at a moderate computational cost.

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