

Origin of the transition entropy in vanadium dioxide

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The reversible metal-insulator transition in VO₂ at $T_c \approx 340$ K has been closely scrutinized yet its thermodynamic origin remains ambiguous. We discuss the origin of the transition entropy by calculating the electron and phonon contributions at T_c using density functional theory. The vibration frequencies are obtained from harmonic phonon calculations, with the soft modes that are imaginary at zero temperature renormalized to real values at T_c using experimental information from diffuse x-ray scattering at high-symmetry wave vectors. Gaussian process regression is used to infer the transformed frequencies for wave vectors across the whole Brillouin zone, and in turn compute the finite temperature phonon partition function to predict transition thermodynamics. Using this method, we predict the phase transition in VO₂ is driven 5 to 1 by phonon entropy over electronic entropy, and predict a total transition entropy that agrees (within 5%) with the calorimetric value.

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I. INTRODUCTION

The first-order phase transition in VO₂ occurs at a temperature of $T_c \approx 340$ K, and is coupled to defect concentration [1–6], strain field [7–9], electric field [10], and optical fluence [11,12]. The transition has been studied since Klemm and Grimm in the 1930s [13], Cook in the 1940s [14], and in detail by Morin in 1959 [15]. Fundamental questions on the nature of the transition have been debated for decades [16–19], and continue to be researched [20–22]. The transition occurs most notably in temperature so understanding the thermodynamic origin is a point of basic importance.

In this study we use density functional theory (DFT) to predict the origin of the VO₂ transition entropy. The applicability of DFT to describe the transition metal oxide class of solids depends sensitively on technical details [23,24]. We use non-spin-polarized calculations based on the PBE exchange correlation functional [25], with on-site Coulomb correction $U_{\text{eff}} = 3$ eV [26]. As shown in Fig. 1, this approach leads to agreement with experiment on the following important points:

(1) Electronic structure—the high-symmetry metallic *R* phase is appropriately gapless. Band gap is opened smoothly with V-V dimerization, resulting in a semiconducting monoclinic (*M1*) phase.

(2) Transition enthalpy—the low-temperature *M1* phase is energetically favored over the high-temperature *R* phase [27].

(3) Mechanical stability—the low-symmetry *M1* phase is stable against distortion and the high-symmetry *R* phase is unstable in 0-K DFT simulation.

Including spin polarization is shown in Fig. 1 to lower the DFT energy of *R*-VO₂ with respect to the nonmagnetic solution, destroying agreement with experiment for the points

listed above. The problems related with spin polarization in the DFT description of VO₂ have been discussed before [28], and have been resolved fully only in the context of quantum Monte Carlo simulations [20], which are too computationally expensive to use to investigate lattice dynamics. We therefore take the pragmatic approach employed by other authors of using nonmagnetic calculations [29], on the basis of their agreement with experiment.

For the *M1* phase, the Born-Oppenheimer surface is convex about equilibrium coordinates. The harmonic approximation to the interatomic potential is appropriate for small displacements, and is expected to be adequate for *M1*-VO₂ up to T_c . On the other hand the high-symmetry *R* phase has negative second-order force constants which qualitatively invalidate free-energy predictions at the harmonic level. Approaches to remedy this that include anharmonic effects have become more accessible thanks to recent developments [30–35], enabling the description of systems with light atoms, at ultrahigh temperatures, or near phase transitions, yet widespread application of first-principles anharmonic thermodynamics remains limited due to computational cost and complexity. In this work we present a simple, experimentally motivated approach to compute the thermodynamics of temperature-stabilized imaginary modes in VO₂. The method is low cost and applicable generally to the DFT thermodynamics of high-temperature phases that are unstable at zero temperature.

II. SOFT MODE THEORETICAL APPROACH

In the soft mode theory of Cochran and in Landau phenomenological approaches [37–40], a square-root temperature dependence is identified for transition parameters. The squared frequency ω_{iq}^2 of a mode *i* that softens near the transition at wave vector **q** is expected to decrease

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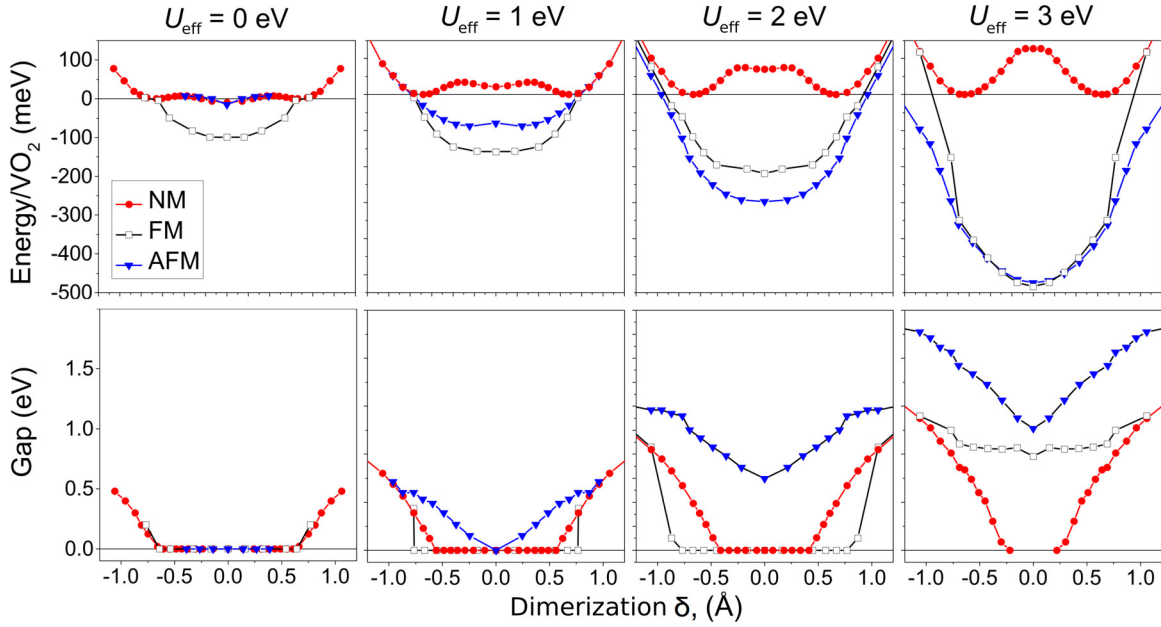


FIG. 1. Potential-energy surface (eV/VO₂) and band gap (eV) as a function of dimerization δ (Å), which is the difference in d (V-V) between consecutive pairs of cations along the rutile c axis. Values are shown for nonmagnetic (NM), antiferromagnetic (AFM), and ferromagnetic (FM) ordering, and for a range of d electron on-site Coulomb interaction strengths, $U_{\text{eff}} = [0, 3]$ eV. The NM $U_{\text{eff}} = 3$ eV description appropriately opens the band gap in dimerization and provides a mechanically unstable high-symmetry phase.

linearly with temperature towards a first-order solid-state transition [41]:

$$\tilde{\omega}_{iq}^2(T) \propto T - T_0. \quad (1)$$

In VO₂ this proportionality has been observed in experimental measurements [36]. For example, Cohen and Terauchi report a linear temperature response from diffuse x-ray-scattering measurements at $\mathbf{q} = \mathbf{R}$ with $\mathbf{R} = \langle \frac{1}{2} 0 \frac{1}{2} \rangle$ which is represented in the left axis in Fig. 2. The temperature T_0 , when $\tilde{\omega}_{i\mathbf{R}} \rightarrow 0$, has a value of $T_0 = 329$ K, and corresponds to the classical second-order transition temperature. Along with the first-order transition temperature T_c , Eq. (1) relates the phonon frequency at 0 K, $\tilde{\omega}_{i\mathbf{R}}^2(0)$, to the frequency at the transition temperature as

$$\tilde{\omega}_{i\mathbf{R}}^2(T_c) = \tilde{\omega}_{i\mathbf{R}}^2(0) \frac{T_c - T_0}{-T_0}. \quad (2)$$

Here the shifted frequency $\tilde{\omega}_{i\mathbf{R}}(0)$ is equal to the harmonic frequency $\omega_{i\mathbf{R}}$ that is calculated with DFT. The application of the transformation of imaginary harmonic DFT frequencies at 0 K to real frequencies at T_c is shown in Fig. 2. The method gives values for the temperature-stabilized frequencies at negligible additional cost to standard harmonic DFT calculations, provided the coefficients T_0 and T_c are known, which is often the case as shown by the experimental data reviewed by Cochran and Cowley [40,41].

To implement the frequency shifts for R -VO₂, the transition modes which are shown in Fig. 2 to be imaginary at \mathbf{R} , \mathbf{Z} , and \mathbf{A} in $q_z = \frac{1}{2}$ are renormalized to T_c following the prescription described in the previous paragraph. At other R -VO₂ wave vectors (see Brillouin-zone geometry, Fig. 3, Appendix B), the frequencies do not soften to imaginary harmonic frequencies. For example, in Fig. 2 the Γ , \mathbf{X} , and \mathbf{M} wave vectors in $q_z = 0$ have real harmonic frequencies at $T = 0$ K. The frequencies

in $q_z = 0$ that do not soften are modelled using the DFT harmonic frequencies ω_{iq} .

In order to make thermodynamic predictions for a high-temperature phase we need to sample the transformed modes finely across the Brillouin zone, not only at the limited high-symmetry \mathbf{q} points in the $q_z = \frac{1}{2}$ and $q_z = 0$ regions described. To obtain $\tilde{\omega}_{iq}(T_c) \in \mathbb{R} \forall i\mathbf{q}$, the partial knowledge we already have of the frequencies transformed to T_c is found to be sufficient data for machine learning techniques to interpolate $\tilde{\omega}_{iq}(T_c)$ to arbitrary phonon wave vectors. $\tilde{\omega}_{iq}(T_c)$ is inferred at all irreducible Brillouin-zone wave vectors using Gaussian process regression (GPR) [42], enabling the partition function of the R -VO₂ vibrational system to be specified at T_c . GPR accuracy benchmarks and technical details are provided in Appendix D.

To understand the source of entropy driving the transition, we compute $S_{\text{DFT}} = S_{\mathbf{R}} - S_{\mathbf{M}1}$ at T_c . $S_{\mathbf{M}1}$ is the DFT harmonic vibrational entropy of $M1$ -VO₂, and for R -VO₂ the entropy is calculated as $S_{\mathbf{R}} = S_{\mathbf{R}}^{\text{el}} + S_{\mathbf{R}}^{\text{ph}} + \tilde{S}_{\mathbf{R}}^{\text{ph}}$ with consecutive terms from electrons, the harmonic phonon entropy, and the soft-mode phonon entropy from the two experimentally renormalized transition modes. Thermodynamic calculation details are provided in Appendix C.

III. RESULTS AND DISCUSSION

The total transition entropy we predict for VO₂ is $S_{\text{DFT}} = 1.42k_{\text{B}}/\text{VO}_2$. The commonly referenced calorimetric value is $S_{\text{exp}} = 1.5k_{\text{B}}/\text{VO}_2$ [43]. Our predicted value of $S_{\text{DFT}} = 1.42k_{\text{B}}/\text{VO}_2$ agrees with the calorimetric value to within 5%. The predicted value is composed of the contributions $S^{\text{el}} = 0.25$ and $S^{\text{ph}} = 1.17k_{\text{B}}/\text{VO}_2$. The source of entropy driving the transition is therefore phonons over electrons at a ratio of almost 5 to 1.

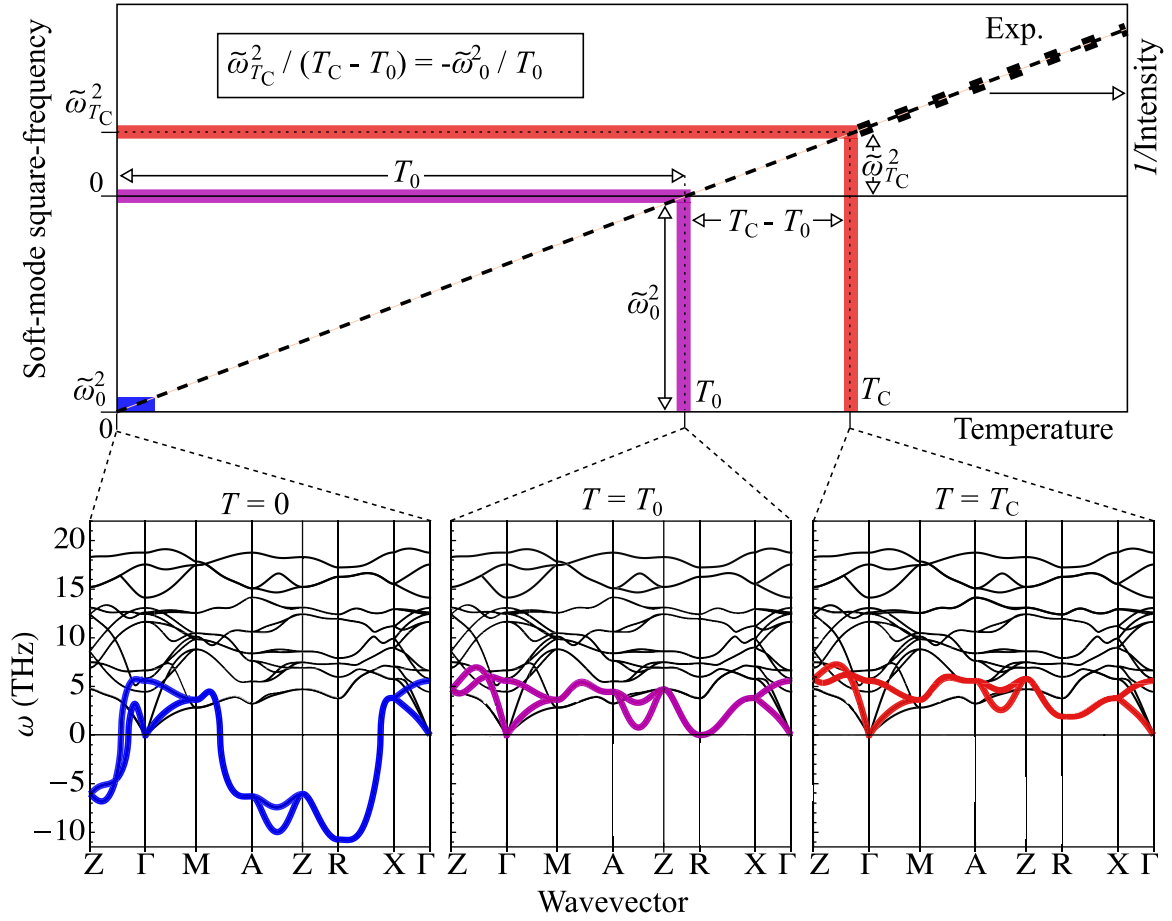


FIG. 2. Top, right axis: Inverse intensity from diffuse x-ray scattering vs temperature [36]. Top, left axis: Linear softening of square frequencies with temperature. The transition occurs at T_c and the classical second-order transition temperature is T_0 . The frequencies at 0 K and T_c , shown as $\tilde{\omega}_0$ and $\tilde{\omega}_{T_c}$, are related linearly. Bottom: DFT phonon dispersion for R -VO₂ at 0 K, T_0 and T_c . Thick colored lines show the soft modes after renormalization, at 0 K (blue), T_0 (magenta), and T_c (red).

In Table I our entropy predictions are compared to 14 recent and historically reported values from the literature. The values range widely, from $S^{\text{el}} = 0.01$ to $0.6k_B/\text{VO}_2$ and $S^{\text{ph}} = 0.64$ to $1.35k_B/\text{VO}_2$. Among the range of predictions, our conclusions align most closely with those of Budai *et al.* [44], with which we agree that the transition thermodynamics are mostly due to phonons. One difference is that Budai *et al.* [44] compute a phonon entropy of $0.93k_B/\text{VO}_2$ compared to $1.17k_B/\text{VO}_2$ here. Their value is based on $U_{\text{eff}} = 0$ eV calculations, whereas this work uses $U_{\text{eff}} = 3$ eV DFT, to ensure a qualitatively correct description of the electron band gap, transition enthalpy, and R -point lattice instability. (Note that the sensitivity of S^{ph} is less than 1% per 0.1 eV of U_{eff} about the appropriate value of $U_{\text{eff}} = 3$ eV, but the $U_{\text{eff}} = 0$ eV description has qualitatively incorrect features.) A second difference with the results of Budai *et al.* [44] concerns their reported “best” predictions, which use a phonon entropy estimate from scattering measurements, which is $1.02 \pm 0.09k_B/\text{VO}_2$, compared to our value of $1.17k_B/\text{VO}_2$. Consequently the error with respect to the total calorimetric value [43] of $1.5 \pm 0.01k_B/\text{VO}_2$ is $0.08k_B/\text{VO}_2$ here, rather than $0.21k_B/\text{VO}_2$ [44].

A controversial point that merits discussion is the possibility of a spin contribution to the transition entropy. Quantum

Monte Carlo calculations have predicted that the R phase, which in nature only exists above T_c , would be spin ordered at $T = 0$ K [20]. On this basis Xia and Chen suggest a spin contribution to the transition entropy [45]. Accounting for a coincident spin disordering at T_c in our predictions increases the entropy value by $\ln(2) = 0.69k_B/\text{VO}_2$ to $S_{\text{DFT}} = S^{\text{el}} + S^{\text{ph}} + S^{\text{spin}} = 0.25 + 1.17 + 0.69 = 2.11k_B/\text{VO}_2$, which exceeds the experimental value of $S_{\text{exp}} = 1.5k_B/\text{VO}_2$. If a $\ln(2)$ spin contribution to the transition entropy exists, S^{ph} must be considerably lower for S_{DFT} to remain consistent with S_{exp} . Considering the neutron-scattering measurements by Budai *et al.* we are inclined to believe this is unlikely [44]. The neutron measured phonon density of states (DOS) can be used to estimate a phonon entropy of $1.02k_B/\text{VO}_2$ (Table I), which is similar to our predicted value of $S^{\text{ph}} = 1.17k_B/\text{VO}_2$, and insufficiently small to accommodate the full spin term. We therefore consider that a fully disordered Heisenberg spin contribution to the transition is unlikely. In order to confirm or refute inferences based on our experimentally renormalized DFT thermodynamics and the neutron-scattering measurements of Budai *et al.* [44], we propose a simple experiment to measure T_c in the presence of a strong magnetic field. If there is a spin contribution to the entropy, it should vanish in the presence of the magnetic field, which will bring the value

TABLE I. Historical measured and computed VO_2 transition entropies, $S(k_B/\text{VO}_2)$, along with available partial electron, phonon, and spin contributions. * Unpublished measurements by Ryder, reported by Berglund *et al.* [43]. § Values determined from analysis of Ryder's measurements [43]. † Mott and Zylbersztein base their analysis on a total transition entropy of $S = 1.6k_B/\text{VO}_2$, mis-citing a Berglund report which has the entropy at $S = 1020 \pm 5 \text{ cal/mol}$ or $S = 1.51 \pm 0.01k_B/\text{VO}_2$, assuming $T = 340.5 \pm 0.5 \text{ K}$.

Source	Method	Entropy contributions			S
		S^{ph}	S^{el}	S^{spin}	
Klemm and Grimm [13], 1939	calorimetry measurements				1.2
Cook [14], 1947	calorimetry measurements				1.50
Kawakubo [46], 1964	calorimetry measurements				1.1
Ryder [43], 1969	calorimetry measurements				$1.51 \pm 0.01^*$
Berglund <i>et al.</i> [43], 1969	analysis of Ryder's heat capacity measurements	1.25§	0.25§		$1.51 \pm 0.01^*$
Paul [47], 1970	parabolic band model calc.		0.15		-
Hearn [48], 1972	1D model calc.	1.17	0.01		1.18
Chandrasekhar <i>et al.</i> [49], 1973	scanning calorimetry measurements				1.65
Zylbersztein and Mott [16], 1975	analysis of magnetic susceptibility measurements	1.02	0.58		$1.6 (1.51)^\dagger$
Pintchovski <i>et al.</i> [50], 1978	calorimetry and electrical resistivity measurements	0.9	0.6		-
Maurer <i>et al.</i> [51], 1999	Debye model fitted to sound velocity measurement	1.35			-
Budai <i>et al.</i> [44], 2014	IXS phonon measurements and DFT electron calc.	1.02 ± 0.09	0.27		1.29 ± 0.09
Budai <i>et al.</i> [44], 2014	DFT ($U = 0 \text{ eV}$) MD and DFT electron calc.	0.93	0.27		1.2
Xia and Chen [45], 2017	compressed sensing DFT phonon and electron calc.	0.64	0.25	0.69	1.58
This work	expt.-renormalized DFT phonon and electrons calc.	1.17	0.25		1.42

of T_c significantly up. If there is no magnetic entropy involved in the transition, T_c should not change or change very little in the presence of the field.

IV. CONCLUSION

We have described the source of entropy driving the VO_2 metal-insulator transition. Our thermodynamic predictions suggest the transition is driven by phonons over electrons at a ratio of $1.17 : 0.25$, and that the computed entropy agrees with the calorimetric entropy value to within 5%. In order to make our predictions we have performed DFT harmonic phonon calculations, in conjunction with an experimentally motivated soft-mode renormalization scheme based on data from x-ray-scattering measurements. The scheme has predicted values of soft-mode frequencies at the transition temperature for high-symmetry points in the Brillouin zone of $R\text{-VO}_2$. The machine learning interpolation method Gaussian process regression was used to infer the soft-mode frequencies across the full Brillouin zone based on the input of frequencies at partial high-symmetry wave vectors. A simple procedure has been proposed to experimentally confirm or refute claims of a spin disorder contribution to the transition entropy.

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APPENDIX A: DFT CALCULATIONS

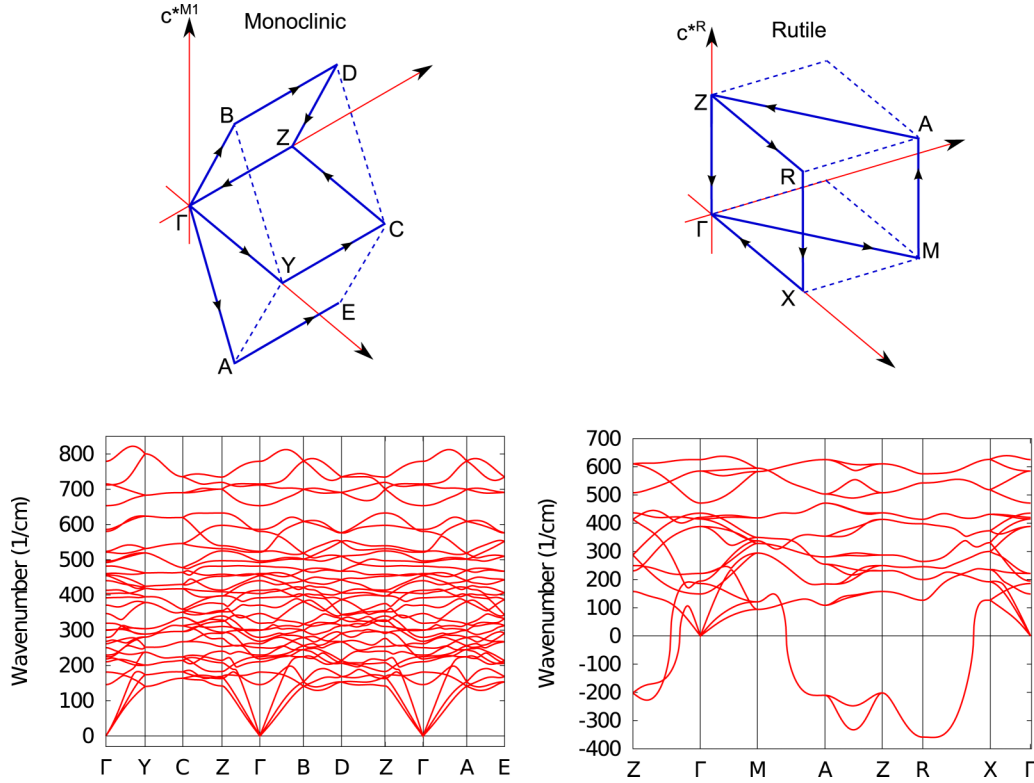
Periodic DFT calculations were performed with the Vienna *Ab-initio* Simulation Package (VASP) [52,53], using the generalized gradient approximation (GGA) in the form of the Perdew-Burke-Ernzerhof exchange-correlation functional (PBE) [25]. The projected augmented wave method was used to describe the interaction between the valence electrons and the core states, which were kept frozen at the atomic references (up to $3p$ in V and $1s$ in O) [54,55]. Plane waves were cut off at a kinetic energy of 520 eV, and \mathbf{k} points were sampled at a density of $6 \times 6 \times 9$ divisions per rutile unit cell. Force and energy convergence thresholds were set to 10^{-3} eV/\AA and 10^{-6} eV respectively.

The Coulomb interaction between vanadium d electrons was corrected with an effective on-site term, U_{eff} [26]. The effect of U_{eff} and magnetic ordering was considered for phase enthalpy and band gap. NM $U_{\text{eff}} = 3 \text{ eV}$ calculations reproduce the basic characteristics well known from experiment, including instability of the high-symmetry $P4_2/mnm$ rutile phase at low temperature, and electronic band-gap phase opening with V-V dimerization.

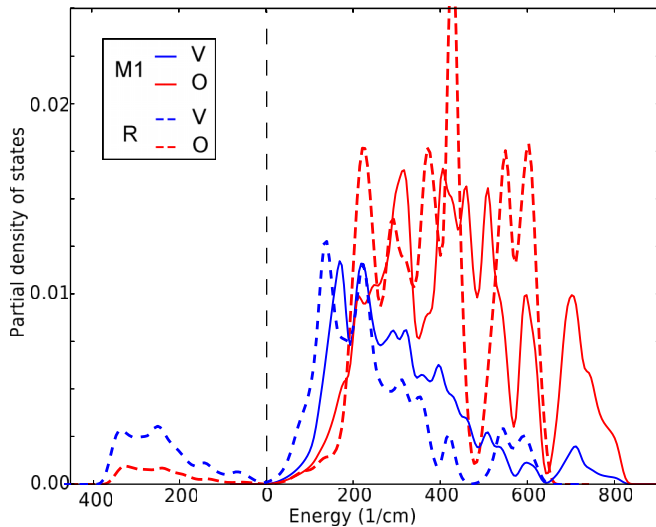
APPENDIX B: PHONON CALCULATIONS

Phonons were computed from second-order force constants using the PHONOPY code [56]. The $M1$ and R phases employ $2 \times 2 \times 2$ and $2 \times 2 \times 3$ supercells respectively. Phonon thermodynamic functions were satisfactorily converged at a sampling density equivalent to $16 \times 16 \times 24 \mathbf{q}$ -point mesh for the rutile conventional unit cell.

Harmonic DFT phonon dispersion is shown in Fig. 3. The Brillouin zones for $M1$ and R unit

FIG. 3. DFT harmonic phonon dispersion for $M1$ and R - VO_2 , and Brillouin-zone sampling paths.

cells are sampled between high-symmetry points in reciprocal space. The path for R - VO_2 follows the sequence $\{Z, \Gamma, M, A, Z, R, X, \Gamma\}$ which corresponds to $\{00\frac{1}{2}, 000, \frac{1}{2}\frac{1}{2}0, \frac{1}{2}\frac{1}{2}\frac{1}{2}, 00\frac{1}{2}, \frac{1}{2}0\frac{1}{2}, \frac{1}{2}00, 000\}$. The path for $M1$ - VO_2 is $\{\Gamma, Y, C, Z, \Gamma, B, D, Z, \Gamma, A, E\}$ which corresponds to $\{000, 0\frac{1}{2}0, \frac{1}{2}\frac{1}{2}0, \frac{1}{2}00, 000, 0\frac{1}{4}\frac{1}{2}, \frac{1}{2}\frac{1}{4}\frac{1}{2}, \frac{1}{2}00, 000, 0\frac{1}{4}\frac{1}{2}, \frac{1}{2}\frac{1}{4}\frac{1}{2}\}$. The phonon densities of states for the $M1$ and R phases are shown projected by atomic species in Fig. 4. The eigenvectors of the imaginary transition modes are shown to project primarily onto the motion of vanadium atoms.

FIG. 4. DFT harmonic phonon density of states for $M1$ and R - VO_2 .

APPENDIX C: THERMODYNAMICS

The phonon entropy difference between the $M1$ and the R phases is estimated from the harmonic free energy

$$S^{\text{ph}} = -\partial_T F^{\text{ph}},$$

where F^{ph} is

$$F^{\text{ph}} = -T \ln Z,$$

and partition function is computed using the harmonic geometric series expression

$$Z = \prod_{i\mathbf{q}} \frac{e^{-\beta\omega_{i\mathbf{q}}/2}}{1 - e^{-\beta\omega_{i\mathbf{q}}}},$$

with $\beta \equiv T^{-1}$.

For the $M1$ phase, entropy is calculated from the standard DFT harmonic frequencies, $\omega_{i\mathbf{q}}$. For the R phase the same expression is applied to the $3n - 2$ real harmonic DFT frequencies that don't soften at the transition, and the two shifted frequencies $\tilde{\omega}_{i\mathbf{q}}$, for the two imaginary harmonic modes subject to the experimental renormalization to real effective frequencies.

The R phase is metallic. As we are only interested in thermal electron excitations at moderate temperatures we assume $\partial_T g(E) = 0$, and that electronic entropy of the R phase can be given in terms of partial one-electron occupancies as

$$S^{\text{el}} = - \int dE g(E) \{f \ln f + (1 - f) \ln(1 - f)\}.$$

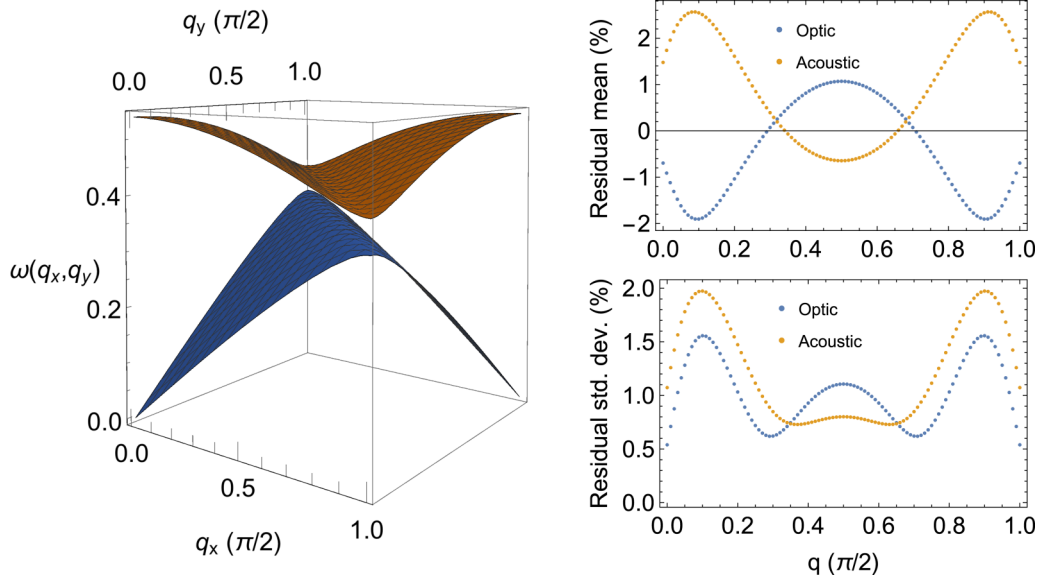


FIG. 5. Right: Analytic dispersion system used to benchmark Gaussian process regression (GPR) performance for Brillouin-zone interpolation from a limited set of initial data points. Left: Mean residual deviation error statistics for the GPR model in the analytic test system.

The total entropy of $M1\text{-VO}_2$ is $S_{M1} = S_{M1}^{\text{ph}}$, and the total entropy for $R\text{-VO}_2$ is $S_R = S_R^{\text{el}} + S_R^{\text{ph}} + \tilde{S}_R^{\text{ph}}$. S_R^{ph} is the vibration contribution from the $3n - 2$ phonon modes that are harmonic at low temperature. \tilde{S}_R^{ph} is from the two bands that soften at the transition and is based on the frequencies transformed to T_c .

APPENDIX D: GAUSSIAN PROCESS REGRESSION

Supervised learning has been used to interpolate phonon frequencies using the nonparametric multivariate Bayesian method Gaussian process regression (GPR) [42]. GPR models can provide an appropriate alternative to Fourier interpolation, which is otherwise the method of choice when the full dynamical matrix is known. Without knowledge of the dynamical matrix at the transition, GPR models can be used to directly interpolate frequencies in \mathbf{q} space from limited $\tilde{\omega}(\mathbf{q})$ data points.

In this work we have used GPR for the \mathbf{q} -space interpolation of the two renormalized soft modes in $R\text{-VO}_2$. The mode frequencies at T_c are determined from experiment at limited high-symmetry wave vectors. GPR can be used to predict how $\tilde{\omega}(\mathbf{q})$ varies across the full Brillouin zone, making possible thermodynamic calculations for the high-temperature phase from limited high-temperature data points. To show that the GPR approach can adequately predict the full $\tilde{\omega}(\mathbf{q})$ surface from limited data points, we benchmark the accuracy of GPR interpolation on an analytic model.

Consider a vanadium-oxygen analytic model with the following dispersion relation:

$$\tilde{\omega}(q_x, q_y) = \sqrt{\left(\frac{1}{m_O} + \frac{1}{m_V}\right) \pm \left\{ \left(\frac{1}{m_O} + \frac{1}{m_V}\right)^2 - \frac{4}{m_O m_V} \sin^2 \mathbf{q} \right\}},$$

which is shown in Fig. 5. The test system includes features such as optic and acoustic-type dispersion, with frequencies that are nonlinear in wave vector in more than one dimension and that have stationary points of inflection. The system is therefore expected to provide meaningful accuracy benchmarks, while also being simple enough to clearly illustrate the method.

To test if the GPR method can reproduce $\tilde{\omega}(q_x, q_y)$ from partial data, we make a training set consisting of 100 points/line along $q_y \in [0, \frac{\pi}{2}]$, at $q_x = 0$ and $q_x = \frac{\pi}{2}$. Root mean square (rms) residual errors of the interpolated system compared to the true system are 5% for the acoustic band and 8% for the optic, with percentages calculated with respect to the maximum frequency value of $\tilde{\omega} = 0.54$ at $\mathbf{q} = 0$. Typically we also know frequency gradients at zone boundaries. For a more realistic test model, derivatives at boundaries are included in the training set. This lowers rms residual errors across \mathbf{q} to 2% and 3% for the acoustic and optic bands respectively.

In the GPR applied in this work, for the soft modes in $R\text{-VO}_2$, an analogous interpolation is made for the two transition bands in $\{q_x, q_y, q_z\}$. Errors of 2% for the interpolated $R\text{-VO}_2$ soft modes correspond to errors of approximately 1% or $0.01k_B/\text{VO}_2$ in the transition entropy difference, which is satisfactory within the scope of this work and in context of other sources of error.

To interpolate the $R\text{-VO}_2$ soft modes we have used a GPR with a nondeterministic radial basis function kernel of the form

$$k(q, q') = \sigma_f^2 \exp \frac{-(q - q')^2}{2l^2} + \sigma_n^2 \delta(q, q'),$$

with Bayesian maximum posterior $\theta = \{\sigma_f, \sigma_n, l\}$ hyperparameters. Training data includes line paths between high-symmetry points in the $q_z = \frac{1}{2}$ and $q_z = 0$ planes, as well as zone-boundary band velocities. GPR training data for soft

modes in the $q_z = \frac{1}{2}$ plane consists of renormalized harmonic frequencies. These are sampled at 100 points/line for each edge in the cycle $\{\mathbf{R}, \mathbf{Z}, \mathbf{A}, \mathbf{R}\}$. For the $q_z = 0$ plane, in which

the transition-mode bands do not soften at the transition, training data consist of 100 points/line samples of the edges in the $\{\mathbf{\Gamma}, \mathbf{X}, \mathbf{M}, \mathbf{\Gamma}\}$ graph for harmonic frequencies.

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