PHYSICAL REVIEW B **102**, 165138 (2020)

Electronic entropy contribution to the metal insulator transition in VO_2

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(Received 11 June 2020; revised 31 August 2020; accepted 1 September 2020; published 21 October 2020)

VO_2 experiences a metal-insulator transition at 340 K. Discontinuities in electronic transport properties, such as the Seebeck coefficient and the electronic conductivity, suggest that there is a significant change in the electronic structure upon metallization. However, the thermodynamic nature of this transformation remains difficult to describe using conventional computational and experimental methods. This has led to disagreement over the relative importance of the change in electronic entropy with respect to the overall transition entropy. A method is presented that links measurable electronic transport properties to the change in electronic state entropy of conduction electrons. The change in electronic entropy is calculated to be 9.2 ± 0.7 J/mol K which accounts for 62%–67% of the total transition entropy. This compares favorably with some estimates of the vibrational entropy.

DOI: 10.1103/PhysRevB.102.165138

I. INTRODUCTION

Morin first reported a metal-insulator transition (MIT) in vanadium dioxide (VO_2). The transition is concomitant with a first order crystallographic transition at $T_t = 340$ K where the high temperature phase is *metallic* [1]. Both the physical nature and thermodynamic driving force of the transition remain controversial. The underlying physics of solids with highly correlated electrons and subsequent implications for electronic devices [2,3] supports further investigation. Herein the thermodynamics of the MIT is of interest, in particular its entropic contribution. Great efforts have recently been reported to compute and quantify the vibrational contribution to entropy in solids. The electron contribution to entropy has remained relegated to computational methods, such as density functional theory [4]. Calculation of the electronic entropy using DFT is difficult in systems with electron correlation because of a lack of accurate exchange-correlation functionals [5]. This is particularly concerning because vanadium dioxide is a material for which exchange-correlation contributes significantly to the system Hamiltonian. There are also no established empirical verification methods for the direct assessment of the accuracy of such functionals in computing the electronic phase transition entropy derived from the electron density of states.

The present work presents a method that evaluates the electronic entropy from electronic transport data. We believe that this method may prove a more accurate measure of the electronic entropy in correlated systems because of the sensitivity of the Seebeck coefficient to changes in the band structure upon phase transition. While it may not apply in a correlated system, the Mott equation highlights this sensitivity to the density of states. Herein we attempt to provide a thermodynamic benchmark for future evaluation of the electronic contribution to the entropy, starting from relatively more readily available experimental data such as electronic transport properties.

Initially, Morin reported a two order of magnitude change in electrical conductivity (σ) in VO_2, with subsequent measurements concluding that this number is between four and five [1]. A discontinuity in the Seebeck coefficient (α) was also reported, despite a relatively constant electron mobility (μ) [6–9]. This suggests that the change in conductivity is almost entirely born by a sharp jump in the number of free carriers in the high temperature, metalized state. The crystallographic symmetry also increases with the transition from a monoclinic structure at low temperature ($P2_1/c$) to a high temperature rutile ($P4_2/mnm$), with a small (0.2%) change in the unit cell volume upon transition (17.78–17.8191 cm^3/mol) [10–12].

The initial variability in the reported electronic transport properties seem to be tied to synthesis and experimental methods. Morin admits that two-probe measurement methods for conductivity call his absolute values into question. Additionally, the large carrier concentration in the high temperature metallic phase makes the evaluation of the electronic mobility difficult due to low voltages in any Hall-type measurement. Furthermore, order of magnitude changes in all electronic transport properties have been reported as a function of oxygen partial pressure; off stoichiometry significantly impacts the measured properties [6,13,14]. Many of these issues have since been rectified, and measurements, such as those by Ruzmetov, use magnetic fields up to 12 T in order to improve the signal to noise ratio of Hall measurements in sputtered thin-film samples [9].

Disagreements over the physical nature of the transition was initially well summarized by Adler and expanded upon by Goodenough [15,16]. Discussions focused on crystal symmetry changes, antiferromagnetic, and electronic correlations (e.g., Mott transition) and others (e.g., Pierels transition) as mechanistic explanations for the phase transition. Goodenough went as far as to propose that multiple mechanisms could occur simultaneously. He demonstrated that there were two distinguishable mechanisms for the MIT in VO_2; an

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antiferroelectric-to-paraelectric transition at a temperature T_t, and a change from homopolar to metallic V-V bonding at T_t'. It would happen that these transitions occur at the same temperature in pure VO_2. However, a $T_t < T_t'$ may be induced by atomic substitutions.

Experiments have verified that the MIT can be tuned in doped VO_2. In thin films of $Ga_xV_{1-x}O_2$, Pintchovski *et al.* demonstrated that the thermodynamic of the phase transition is quantitatively affected by the metallic character of the high temperature phase as modified by the Ga content (x) [17]. This suggests that the metal-insulator transition is largely driven by changes in the electronic structure.

The thermodynamic nature of phase transition remains a controversial topic. A constant temperature and constant pressure phase transition calls for continuity of the Gibbs energy of VO_2, and at equilibrium one relates the enthalpy difference between the insulator and metal phases ($\Delta H^{\mathrm{I}\rightarrow\mathrm{M}}$) to the transition temperature T_t and the entropy of the transition ($\Delta S^{\mathrm{I}\rightarrow\mathrm{M}}$) following:

$$\Delta H^{\mathrm{I}\rightarrow\mathrm{M}} = T_t \Delta S^{\mathrm{I}\rightarrow\mathrm{M}}. \tag{1}$$

Characterization of the enthalpy term has been quite extensive and as synthesis methods have improved, the measured enthalpy of transition has only continued to increase. Current estimates range between 4686–5000 J/mol [18,19]. This is consistent with the effect of impurities in VO_2 nearly universally decreasing the observed transition enthalpy. Larger reported enthalpy values are likely indicative of higher purity samples. The range of reported enthalpy values leads to an entropy of transition between 13.78–14.7 J/mol K at a critical temperature of 340 K for VO_2. Most of the controversy over the thermodynamic nature of the transition is then confined to the study of the magnitude and nature of this entropy term. It contains multiple components relating to the difference in electronic (ΔS_{e}), magnetic (ΔS_{mag}), and vibrational (ΔS_{vib}) degrees of freedom between each phase:

$$\Delta S^{\mathrm{I}\rightarrow\mathrm{M}} = \Delta S_{\mathrm{e}} + \Delta S_{\mathrm{vib}} + \Delta S_{\mathrm{mag}}. \tag{2}$$

It is hypothesized that drastic changes in the bonding characteristic during MITs have significant impact on the electronic degrees of freedom between the insulating and metallic state, leading to significant changes in the electronic entropy [17,20].

Contemporary efforts to measure the phonon density of states using neutron scattering experiments and subsequent calculation of the vibrational and electronic entropy lead to a value of $\Delta S_{\mathrm{vib}} = 8.48$ J/mol K and $\Delta S_{\mathrm{e}} = 2.24$ J/mol K [21]. The electronic entropy computed here uses the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional to calculate the electronic density of states, the integration of which provides the total electronic state entropy. The results of this recent report contradict prior assessments by Pintchovski and Mott that the electronic entropy could be anywhere from 30% to 60% of the total phase transition (and line up more with Guggenheim's theory that the transition was largely a lattice driven phenomenon [6,17,20]).

An examination of the electron thermodynamics could prove useful in deconvoluting the significance of the electronic transition and provide researchers with a thermodynamic benchmark to compare the measurement and calculation of the other components in Eq. (2). The present work proposes to evaluate the change in the electronic entropy across the MIT in VO_2 using a formalism that connects reversible thermodynamics to transport properties. It shows that the electronic contribution to the entropy can be quantified based on established experimental measurement of the transport properties, and that prior assessments of the electron contribution to the entropy of the MIT were underestimates.

II. METHODS AND RESULTS

Accessing the electronic entropy from transport properties has been proposed using the partial molar entropy of electrons, as evaluated from [22,23]

$$\left(\frac{dS}{dn_e}\right)_{T,P,n_j} = -\alpha F, \tag{3}$$

where α is the Seebeck coefficient and F is Faraday constant.

An integral form of this equation, applicable to materials at equilibrium, was derived [24,25] and resulted in the formulation of the electronic state entropy:

$$S_{\mathrm{e}} = -n_e e \alpha_e + n_h e \alpha_h, \tag{4}$$

where e is the fundamental charge, n_i is the number of free charge carriers (here electrons and holes), and α_i are their respective Seebeck coefficients. Since electrons are the primary charge carrier in VO_2, we use only the first term in Eq. (4). Converting from entropy per cubic meter to entropy per mole, and establishing the difference in entropy between the metal and insulator phases, leads explicitly to

$$\Delta S_{\mathrm{e}}^{\mathrm{I}\rightarrow\mathrm{M}} = \left(-n_e^{\mathrm{M}} e \alpha^{\mathrm{M}} V_m^{\mathrm{M}}\right) - \left(-n_e^{\mathrm{I}} e \alpha^{\mathrm{I}} V_m^{\mathrm{I}}\right), \tag{5}$$

where the $V_m^{\mathrm{M,I}}$ represent the molar volume of the metal or insulating phases.

We used values for the free charge carrier concentration as measured by Ruzmetov and characteristic values of the Seebeck coefficient measurement perpendicular to the crystallographic c axis were sourced from Berglund and Cao *et al.* [6,7,9]. The calculated electronic state entropy change is 9.2 ± 0.7 J/mol K (see the Supplemental Material [26] for numerical values used herein).

This would account for 62%–67% of the total reported entropy of transition as evaluated from Eq. (1). Verifying the validity of Eq. (5) as applied to VO_2 is conducted using experimental results for Ga-doped VO_2 from Pintchovski. Gallium is a suitable substituting element, since Ga^{3+} is thought to remove two valence electrons per atom while also maintaining V^{4+} as the sole paramagnetic ion, thereby decreasing possible changes in the magnetic state entropy.

Pintchovski *et al.* measured the resistivity of Ga-doped VO_2 as a function of temperature and Ga concentration, as reproduced in Fig. 1. The transition temperature slightly increases with increasing Ga concentration. Increasing Ga concentration resulted in a decrease of the metallic character of the high temperature phase. As the Ga concentration is increased, the resistivity of both the metal and insulator phase increases, with the metallic phase experiencing a relatively more dramatic change leading to a decrease in the relative conductivity differences. Pintchovski *et al.* also measured the

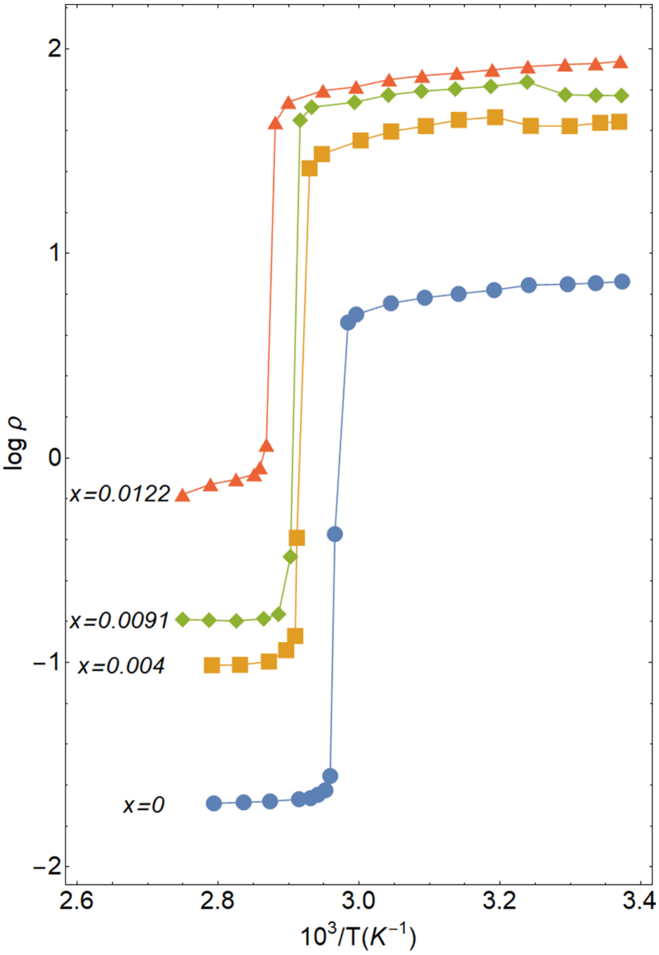

FIG. 1. Resistivity as a function of temperature for various compositions of $Ga_xV_{1-x}O_2$. Reproduced from Ref. [17].

change in enthalpy for the transition, which is shown in Fig. 2 as a function of the relative resistivity difference [17].

Figure 2 shows the enthalpy of transition can be extrapolated to the case where both phases exhibit the same resistivity, leading to ≈1700 J/mol. This can be considered to represent the enthalpy of transition for VO_2 at 340 K *without the accompanying insulator to metal transition*. The resulting estimated vibrational entropy of transition is 5 J/mol K. Added to the electronic state entropy calculation from Eq. (5), the total estimated entropy of the MIT for VO_2 would be 14.22 J/mol K. The results of this analysis are summarized in Table I.

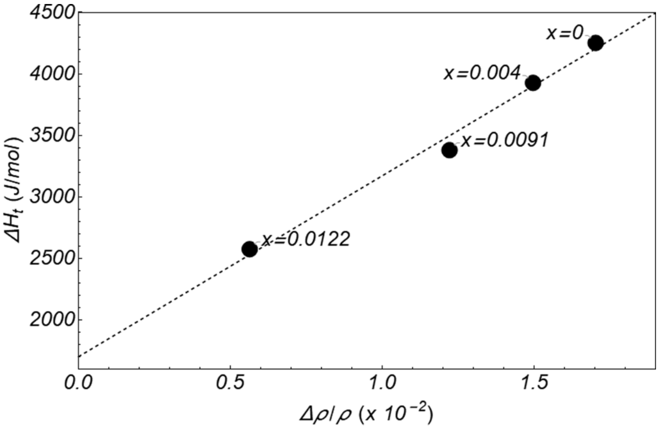

FIG. 2. Enthalpy of transition of various compositions plotted against their change in resistivity upon the insulator to metal phase transition. Reproduced from Ref. [17].

The error reported herein accounts for the uncertainty in the measurements used to calculate electronic entropy. Where standard deviations are provided in the data, these are included explicitly. Otherwise, the uncertainty is assumed to reside within the final significant digit. The error resulting from measurement precision was found to be roughly 8%.

III. DISCUSSION

This study used a formalism whose utility was previously shown for molten systems when calculating the properties of semiconductors that experienced metallization [24,25]. There it demonstrated that the electronic state entropy for molten semiconductors as calculated from Eq. (4) accounted for almost the entire entropy of mixing of the liquid phase. This enables calculating miscibility gaps or metallization temperatures for such liquids.

In the present work a similar framework applied to solid VO_2 enables us to calculate a change in the electronic entropy as a function of experimentally measurable data for a first order solid-state phase transition that is accompanied by an insulator to metal transition. The result suggests that the electronic entropy contribution is quite large for VO_2. This electronic entropy, if added to the contribution experimentally inferred from the study of the role of dopants, provide a total entropy for the transition that is in agreement with the reported total enthalpy and temperature of the transition.

Conventional approaches focus on vibrational contributions to entropy. Budai *et al.* measured the phonon density of states and directly calculated the vibrational entropy component as 8.47 J/mol K [21]. They reported the contribution of electronic entropy to be of the order of 2.24 J/mol K. In addition, the total entropy of transition reported in their study was 12.47 J/mol K; slightly smaller than the range reported elsewhere in the literature. They suggest the remnant 1.746 J/mol K is associated with potential magnetic changes across the transition.

Such observation would have important consequences on an ongoing hypothesis suggested by Mellan *et al.* and others [5,27]; the loss of spin coupling in the metalized state may add an additional component to the entropy. If this was verified, two possibilities arise. Either the existence of a significant magnetic contribution implies some electronic degrees of freedom in the insulator are not captured by the proposed Seebeck-based formalism. This would reduce the total calculated electronic entropy with the current formalism and provide room for such a spin contribution. Alternatively, as reported for strongly correlated oxides, the electronic spin entropy dominates the entropy current and its impact is reflected in the Seebeck measurements. This would imply that the current formalism may already be considering the magnetic entropy.

Budai *et al.*'s calculations did not demonstrate the significance of an on-site vanadium electron-electron interaction

TABLE I. Calculation of the electronic and vibrational entropies are compared to measured results.

n^{M} (cm^{-3})	n^{I} (cm^{-3})	α^{M} (μV/K)	α^{I} (μV/K)	$V_{\mathrm{m}}^{\mathrm{I}}$ (cm^3/mol)	$V_{\mathrm{m}}^{\mathrm{M}}$ (cm^3/mol)	$\Delta H^{\mathrm{I}\rightarrow\mathrm{M}}$ (kJ/mol)	$\Delta S^{\mathrm{I}\rightarrow\mathrm{M}}$ (J/mol K)	ΔS_{e} (J/mol K)	ΔS_{vib} (J/mol K)
1.4×10^{23}	1.1×10^{19}	-23.1 ± 0.2	-400	17.7	17.781	4.686–5	13.782–14.70, 14.2 ± 0.8	9.2 ± 0.7	5.0 ± 0.1
[9]	[9]	[6]	[6]	[10]	[11]	[18,19]	[18,19], This work	This work	[17]

term [21]. Even when such terms are included, as in Mellan *et al.*, it is stated in their work that this term was chosen to ensure that the electron band gap of the insulating phase and enthalpy of transition were qualitatively correct [5].

Our finding is not yet compatible with the upper-bound estimates presented in these recent works. Since the prior work on the total entropy of the transition did not have empirical access to the electronic entropy, the consistency of using electronic transport properties and the proposed method summarized by Eq. (5) warrant discussion.

The nonelectronic component of the entropy of transition was estimated from the experimental measurements of changes in electrical conduction and the transition temperature and enthalpy with substitution of V with Ga. The extrapolation of the trends in enthalpy in Fig. 2 to the case where there is no change in resistivity upon the transition can reasonably be assumed as the lattice contribution to the entropy change; itself a difficult quantity to measure. This assumption is in agreement with Eq. (5). As the resistivity of the metalized state increases, the difference in resistivity between the metal and insulator shrinks with a commensurate reduction in the number of free carriers in the metalized state. This corresponds to a reduction in the electronic contribution to the entropy, thereby leaving the remaining entropy change a function of the lattice.

Calorimetric data from Pintchovski further supports this line of thinking; the entropy of transition of the MIT declined by 42% with a Ga concentration of 1.2%. Each Ga^{3+} ions should remove two free electrons from the system by causing vanadium to form V^{5+} as charge compensating defects, a qualitative picture that supports the increase in resistivity with increasing Ga content presented in Fig. 1 [17].

VO_2 has also been doped with other elements like Cr, which can be expected to enter VO_2 as Cr^{3+} and result in a similar reduction in free carrier concentration. Reports of a reduction in the enthalpy of the transition with limited change in the critical temperature of the MIT would indicate an effect in $\mathrm{Cr}_x\mathrm{V}_{1-x}\mathrm{O}_2$ [28]. Cr presents an additional convolution, as Cr^{3+} possesses an electronic structure $[\mathrm{Ar}]3d^3$, which likely influences the magnetic entropy of the two phases. Quantitative assessment of these effects in the $\mathrm{Ga}_x\mathrm{V}_{1-x}\mathrm{O}_2$ and $\mathrm{Cr}_x\mathrm{V}_{1-x}\mathrm{O}_2$ alloys would benefit from Seebeck measurements as a function of Ga and Cr concentration and temperature. However, in order to isolate the electronic entropy effects, only calorimetric data from Ga doped samples were considered.

One would expect other dopants like Ti, Nb, and Mo to cause similar reductions in the free electron concentration and indeed these materials induce a decrease in the enthalpy of transition in VO_2 [29]. However, the behavior of these dopants has proven more complex, introducing the formation of a non-negligible number of holes and lattice defects such as oxygen vacancies. Thus, quantitative application of the electronic entropy formalism would require care to identify the contribution of the electronic carriers to the total transport properties.

There may be additional electronic degrees of freedom for the insulating state that are not captured in Eq. (5). One can consider the electronic entropy term in Eq. (2) to be composed of two separate electronic contributions. The first, as presented here, would be the transport electronic entropy that is primarily concerned with the entropic contributions of conduction electrons. It has been suggested by others that there may exist additional configurational electronic degrees of freedom in the insulating phases of materials [30]. Additional electronic degrees of freedom in the insulating state would imply the present calculation is missing an additional term in Eq. (2) that would decrease the overall entropy of transition. Even subtracting a couple J/mol K from the electronic entropy difference would still leave the electronic state change the dominant entropic contribution to the MIT.

Nevertheless, the results presented herein increase the confidence that focus on the entropy of conduction electrons is sound, as our calculation of the total entropy of transformation does not preclude the possibility of additional electronic degrees of freedom in the insulating phase of VO_2.

IV. CONCLUSION

A method for calculating the electronic contribution to the metal-insulator transition entropy of VO_2 has been applied. ΔS_{e} was calculated to be 9.2 ± 0.7 J/mol K, representing 62%–67% of the transition entropy. A thermodynamic explanation for the observed reduction in the entropy of transition of some vanadium based oxides with a commensurate reduction of the free carrier concentration in the metalized state has been supported. Additionally, the successful treatment of the conduction electrons as individual particles with fundamental unit charge suggests that the electron correlation is weakened in the metallic state. This analysis also suggests that the transition is more Mott in character as it is more heavily dominated by the electronic contribution to the entropy of the MIT [31,32].

ACKNOWLEDGMENTS

We would like to thank E. Pang for some fruitful discussions around the interesting nature of the martensitic phase transition in VO_2. This material is based upon work supported by the Air Force Office of Scientific Research under Award No. FA9550-20-1-0163.

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