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Systematics in the metal-insulator transition temperatures in vanadium oxides

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ABSTRACT

Nine of the known vanadium oxides, $\text{VO}_{2-1/n}$ (n – a positive or negative integer) with $n = 2-6, 8, 9, \infty$ and -6 , undergo metal-insulator transitions accompanied by structural transitions, at various temperatures T_{MIT} (V_7O_{13} is metallic above $T=0$). Among the persistent efforts to determine the driving force (s) of these transitions, electron–electron (Mott-like) and electron–phonon (Peierls-like) interactions, there were several attempts to find systematics in T_{MIT} as function of n . Here we present an unexpectedly simple and illuminating systematics that holds for positive n : if T_{MIT} is the absolute value of the difference between $T_M(n)$ and $T_P(n)$, which represent the contributions of electron–electron and electron–phonon interactions, respectively, all data points of T_M-T_P versus $1/n$ lie on, or close to, two simple straight lines; one is $T_M-T_P = T_\infty(7/n-1)$ for V_3O_5 , V_4O_7 , V_5O_9 , V_7O_{13} , V_8O_{15} , V_9O_{17} and VO_2 and the other is $T_M-T_P = T_\infty(3/n-1)$ for V_2O_3 , V_6O_{11} and VO_2 .

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1. Introduction

The general formula $\text{VO}_{2-1/n}$ (n – a positive or negative integer) represents all known vanadium oxides. The monovalent members of the family with $n=1$ (VO) and $n=-2$ (V_2O_5) are metallic and semiconducting at all temperatures, respectively. The monovalent oxides with $n=2$ (V_2O_3) and $n=\infty$ (VO_2) and the mixed valent oxides with $n=3-6, 8, 9$ and -6 , undergo metal-insulator transitions (MIT) accompanied by structural transitions, at various temperatures, T_{MIT} , below and above room temperature. The mixed valence compounds with positive n belong to the so-called Magneli phases and those with negative n – to Wadsley phases. These transitions, including the absence of a transition for $n=7$, have attracted attention over many decades. One of the subjects under debate for more than half a century, was the role of the electron–electron (Mott-like) and electron–phonon (Peierls-like) interactions in these transitions [1–3]. Along with the efforts to understand the nature of these phase transitions there have been several attempts to find a systematic behavior of T_{MIT} as function of n . In 1971, when only the T_{MIT} of the Magneli phases with $n=4-8$ were known, Nagasawa [4] showed that (1) Magneli phases are classified into two groups by the transition temperatures in which

one has even n and the other odd n and (2) transition temperatures decrease with the increase of even and odd n (the line for the two odd n lies below that connecting the three for even n). In 1980 [5], using data from References [6,7] for $n < 8$ we showed that T_{MIT} plotted versus $1/n$ lie on, or close to several straight lines as shown below:

- (a) $T_{MIT} = T_{MIT}(\infty)(1 - 1/n)$ for $n = 1, 2, 4$ and ∞ ,
- (b) $T_{MIT} = T_{MIT}(\infty)(1 - 3/n)$ for $n = 5, 6$ and ∞ ,
- (c) $T_{MIT} = T_{MIT}(\infty)(7/n - 1)$ for $n = 3, 4, 5$ and 7 ,

where $T_{MIT}(\infty) = T_{MIT}(\text{VO}_2)$. Note that the lines (a) and (c) cross at $1/n = 1/4$ and that the lines (a) and (b) meet at $1/n = 0$. The then available data hinted at the existence of another simple line, (d) $T_{MIT} = T_{MIT}(\infty)(1 - 7/n)$ (the reflection of (c) about the vertical axis $1/n = 1/7$) for $n = 7, 8$ and ∞ , but the discrepancy of the data point for $n=8$ was far too large in view of the close agreement of the points in (a)–(c). At that time, the metallic nature of VO was still problematic, its non-metallic conductivity being governed by the large concentration of native defects. In 2007 experimental and computational evidences were presented in support of VO being a strongly correlated metal [8]. The attempt to include the solitary data point with negative n ($n = -6$) in the systematics is ignored here.

The renewed inspection of the systematics was motivated by later reports in the literature, including $T_{MIT}(\text{V}_9\text{O}_{17})$ [9,10,2] which strengthened confidence in the previously reported systematics.

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Two questions were asked at this stage: (1) How valid are these simple lines? (2) If they are valid, what do they imply?

In order to answer the first question, a wide spread of $T_{MIT}(x)$ data, where $x = 2 - 1/n$, obtained over the years by many groups from electrical and magnetic measurements were tabulated and plotted; these data include thermal hysteresis and experimental errors. Appendix A is devoted to the verification of these lines.

The so-proven validity of the data used in References [1,2,5] and the present understanding in the field allowed a revision of the interpretation of T_{MIT} that simplified the systematics to being expressed by only two straight lines.

2. Transition temperatures of VO_x

The transition temperatures of the vanadium oxides shown in Table 1 were taken mainly from Reference [6]; the data missing in that early article were filled in from more recent publications. Graphs of $T_{MIT}(x)$ using data from this Table appear in research articles and reviews related to VO_x such as [1,2,11]. A similar graph including also the datum for V_9O_{17} as in [2], is shown in Fig. 1 where the primary and secondary horizontal axes have been extended to $x=1$ and $n=1$. Solid lines connect the data points as in the above references. The four dashed straight lines which in part overlap with the solid lines represent (a)–(d), their expressions shown in the previous section. The datum for V_9O_{17} was available in 1981 but was ignored in the literature until 2013. As in [5], the point for V_8O_{15} deviates significantly from line (d) and that for V_3O_5 deviates slightly from line (c) (430 K instead of 453 K).

The most interesting pair of lines in Fig. 1 is of course the (c) and (d) pair, for which $T_{MIT} = \pm 340(7/n - 1)K$; these two lines contain most of the data points for T_{MIT} from $n=3$ to $n=\infty$. Thus, if the line representing $T_{MIT} = 340(1 - 7/n)K$ and the points laying on it (including that for $n=8$) are rotated around the horizontal axis, all the points of the (c) and (d) pair lie now on a single straight line with the point for $n=8$ close to it. This simple transformation leaves out two points on what previously was line (a) ($1/n = 1/2$ and 1) and one point on the former line (b) ($n=1/6$). If the point for $n=1/6$ is reflected about the horizontal axis we obtain a new straight line that connects the points for $1/n=1/2$, $1/n=1/6$ and $1/n=0$. It turns out that the ordinate of the new graph represents the difference between two functions, while that of the old graph represents the absolute value of this difference. And indeed, the zero for V_7O_{13} is not a minimum but a crossover point. The most suitable names for the two functions are T_M and T_P (M for Mott and P for Peierls). The data points in Fig. 2 represent $T_M - T_P$ versus $1/n$ for all V_nO_{2n-1} with $n > 1$; the solid lines are the fitted linear trendlines with their Paterson correlation coefficients. The dashed lines represent the ideal relations $T_M - T_P = 340(7/n - 1)K$ and $T_M - T_P = 340(3/n - 1)K$. The upper dashed line is distinguishable but still very close to the solid line. The lower dashed line is indistinguishable on the scale of Fig. 2,

Table 1
Vanadium oxides V_nO_{2n-1} (positive n) and their M-I transition temperatures.

n	V_nO_{2n-1}	T_{MIT} (K)	Reference
1	VO	Metallic	[8]
2	V_2O_3	168	Table in [6]
3	V_3O_5	430	[7]
4	V_4O_7	250	Table in [6]
5	V_5O_9	135	Table in [6]
6	V_6O_{11}	170	Table in [6]
7	V_7O_{13}	Metallic	[6]
8	V_8O_{15}	70	Table in [6]
9	V_9O_{17}	79	[10]
∞	VO_2	340	Table in [6]

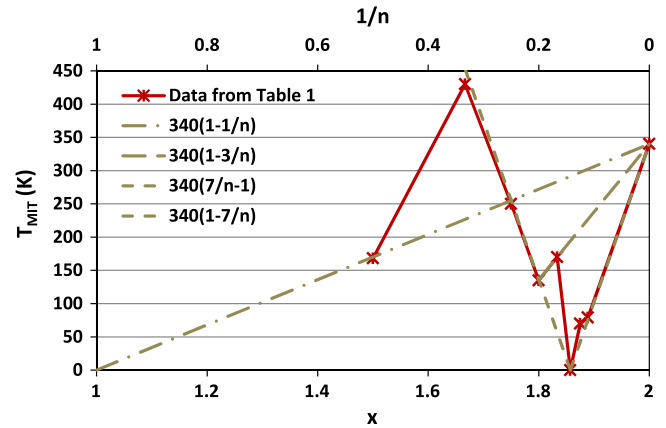


Fig. 1. (Color online) T_{MIT} as function of x (primary horizontal axis) and $1/n$ (secondary horizontal axis). Symbols represent data from Table 1 connected by solid lines and dashed lines represent the systematics.

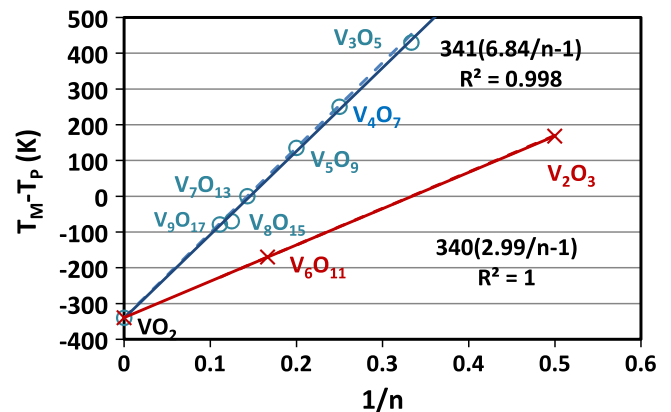


Fig. 2. (Color online) $T_M - T_P$ as function of $1/n$. Symbols represent data points, solid lines represent linear trendlines fitted to the data and dashed lines represent the two simple expressions of $T_M - T_P$. Note that the lower dashed line is indistinguishable from the corresponding solid line.

it overlaps the corresponding solid line. The point for $n=1$ (VO) remains isolated; the extrapolation of line (a) in Fig. 1 to 0 for $n=1$ is not understood.

3. Discussion

The discussion on the MIT in V_nO_{2n-1} is based on essentials of the state of the art of this topic as described in References [1,2]. The rutile VO_2 structure contains pairs of translationally distinct but symmetry equivalent, parallel, infinite chains of edge sharing octahedra. In V_nO_{2n-1} the chains are broken into n -octahedra long units; the symmetry is broken in such a way that rutile-like chain fragments are connected by corundum-like (V_2O_3 -like) chain ends. The two parallel chains become symmetry inequivalent and are denoted in [2] as “A” and “B”. Theoretical calculations for several V_nO_{2n-1} compounds [1] showed that electron-lattice interactions are largest in the centers of the chain-fragments while electron-electron interactions are largest at the fragments’ ends. Recent experiments [12] confirm the importance of electron-electron correlations in V_3O_5 (the highest point of Fig. 2). With increasing n the electron-lattice interaction increases while the electron-electron interaction decreases. The absence of transition in V_7O_{13} is probably due to mutual cancellation. For V_2O_3 $T_M > T_P$; this is not surprising since this material was originally considered a canonical Mott system. The location of VO_2 at the bottom of Fig. 2 is also not

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