

Metal-insulator transition in V_4O_7 : Specific-heat measurements and interpretation

B. F. Griffing,* S. A. Shivashankar,† S. P. Faile,‡ and J. M. Honig

Department of Physics and Department of Chemistry, Purdue University, West Lafayette, Indiana 47907

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Specific heat data are presented for single-crystal platelets of V_4O_7 in the range 5–350 K encompassing both the antiferromagnetic and the metal-insulator transitions. The results, coupled with structural and NMR studies in the literature, suggest that magnetic exchange effects are largely responsible for the existence of cationic chains that are differentiated in charge, and for the metal-insulator transition in this compound.

INTRODUCTION

V_4O_7 is a member of the vanadium Magnéli series V_nO_{2n-1} , whose properties have been repeatedly reviewed.¹⁻⁷ The triclinic V_4O_7 structure is comprised of VO_2 -like blocks that are separated by crystallographic shear planes. Between the shear planes, the V ions form chains, as shown in Fig. 1. The vanadium atoms are approximately octahedrally coordinated by oxygen atoms that form a nearly hexagonally close packed array. V_4O_7 undergoes a metal-insulator transition near 237 K and antiferromagnetic ordering near 34 K. With the exception of V_7O_{13} , all Magnéli compounds exhibit similar

metal-insulator transitions at high temperature, and all such compounds exhibit antiferromagnetic ordering at lower temperatures. The metallic as well as the insulating states of the different Magnéli phases are similar in properties: so, a detailed study of a particular compound can provide information about the entire series. What distinguishes V_4O_7 from the other Magnéli phases¹⁻⁷ is that its metal-insulator ($M-I$) transition at temperature T_{MI} is separated by a substantial temperature range from the antiferromagnetic (AF) ordering transition at the Néel point T_N .^{8,9} This provides a unique opportunity for the separate study of each transition. A variety of physical properties of V_4O_7 , such as resistivity,¹⁰⁻¹⁴ Seebeck coefficient,

V_4O_7

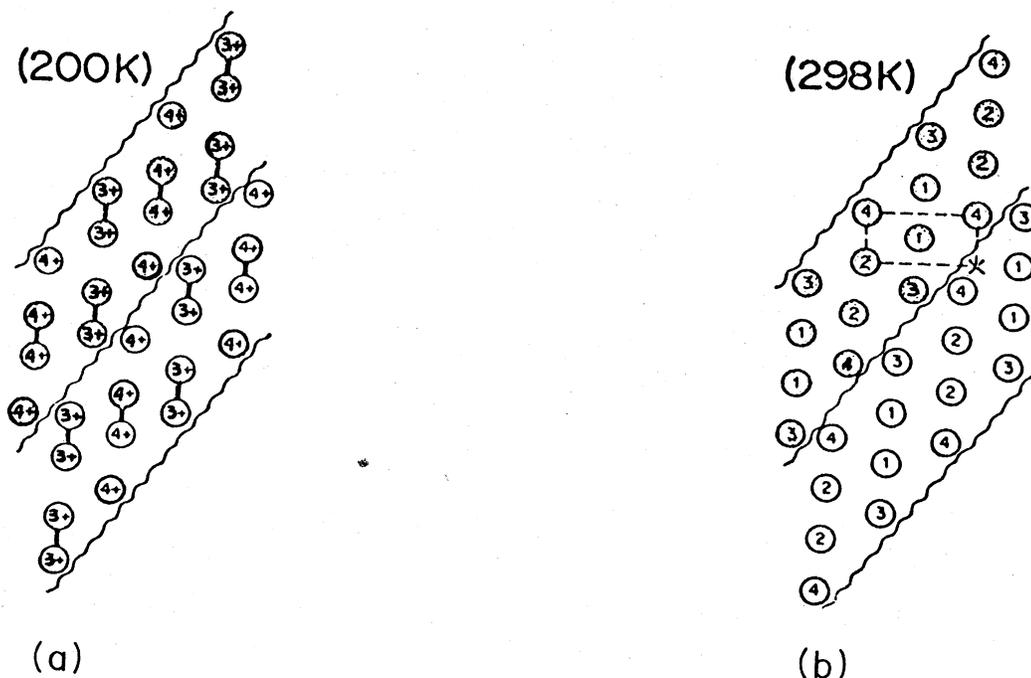


FIG. 1. Pseudorutile sections of V_4O_7 with (110) as horizontal axis and (001) as vertical axis. The wavy lines represent shear planes. Each pseudorutile block steps up relative to the adjacent block across the shear plane which makes an angle of approximately 65° with the plane of the page. The oxygen atoms are deleted for clarity. This figure is taken from Ref. 35.

cient,¹¹ magnetic susceptibility,^{9,15-17} Mössbauer spectra,^{18,19} x-ray-absorption spectra,²⁰ NMR effects,²¹⁻²⁴ optical properties,^{25,26} and ¹⁸O substitutional effects,²⁷ have already been reported over a temperature range up to 350 K. However, a rather fundamental quantity, the specific heat, apparently has not previously been determined in the high-temperature range, although several measurements have been reported below 50 K,^{8,9,28} also, one set of differential thermal analysis (DTA) measurements is available.²⁹ To gain further information about the driving force behind the transition, specific heat measurements were undertaken in the 5–350 K region. As described below, these results led us to postulate a new mechanism for the metal-insulator transition, which invokes changes in the pair-exchange energy near the transition temperature.

EXPERIMENTAL

V₄O₇ platelets were prepared at the Purdue Central Materials Preparation Facility using the vapor transport technique of Nagasawa *et al.*¹² The low-temperature specific heat of the resultant material was measured by Khattak *et al.*⁸ Three pieces from this batch totaling 94 mg were selected to carry out the present specific heat measurements in the 5–330 K range on a relaxation calorimeter of our own design.³⁰ The resulting specific heat is plotted in Figs. 2 and 3. The graphically determined heat and entropy of transition are presented in Table I. No peaks, other than those expected at the metal-insulator transition and at the antiferromagnetic ordering temperature, were observed, confirming that other Magnéli phases were not present in significant amounts. The specific heat measurements between 6 and 50 K are in very good agreement with those reported earlier.^{8,9,28} The Néel temperature $T_N=34.5$ K as determined from Fig. 2 falls within the range 32–40 K quoted in the literature. The metal-insulator transition temperature $T_{MI}=237$ K, as deduced from the maximum value of the heat capacity curve of Fig. 3, compares with a range of 238–250 K cited by other workers.^{2-7,9,13,17,22,25,29} *M-I* transitions monitored by transport measurements generally exhibit a 6- to 8-degree hysteresis;^{3,5,11} by contrast, no significant difference was noted in the intensities of the (251) and (284) reflections,

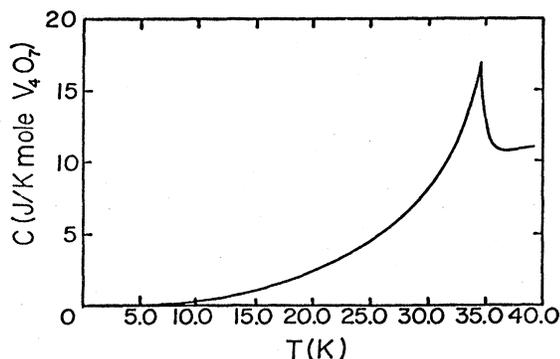


FIG. 2. Specific heat of V₄O₇ in the 0–40 K temperature range. The large peak at 34.5 K is due to the Néel transition.

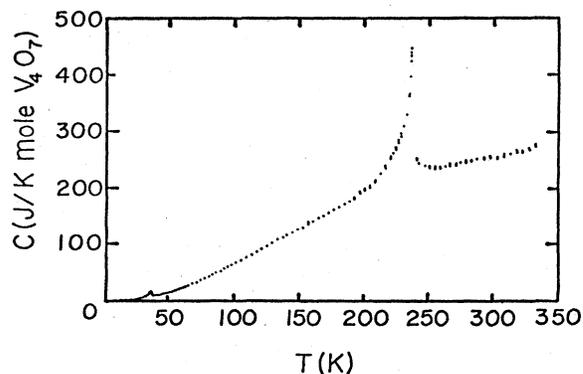


FIG. 3. Specific heat of V₄O₇ in the 0–350 K temperature range. The large peak at 237 K is due to the metal-insulator transition.

obtained by x-ray diffraction measurements as a function of increasing or decreasing temperature.^{11,31} These intensities, as well as the resistivity measurements, indicate that the *MI* transition extends over a wide temperature range of some 100 K and terminates in a weakly first-order fashion near 235 K. In the heat capacity measurements shown in Figs. 2 and 3, the anomaly exhibits the conventional Λ shape and appears to extend over approximately 70 K; no hysteresis effects were observed either at $T=T_N$ or at $T=T_{MI}$. The entropy change at the transition shown in Fig. 2 amounts to 6.0 J/K mole V₄O₇, which is less than 20% of the value anticipated from the complete order-disorder transformation of a magnetic spin with $S=\frac{1}{2}$. This finding correlates with the fact that the effective magnetic moment of V₄O₇ is $(0.5 \pm 0.2)\mu_B$ (μ_B is the Bohr magneton), as compared to the expected value of $2.35\mu_B$.⁹ The low ΔS value undoubtedly reflects the existence of appreciable vanadium-vanadium pairing as described below. The entropy value of 22.0 J/K mole V₄O₇ for the transition at 237 K determined by us compares with values of 9.35 (Ref. 5) and 12.2 (Ref. 13) J/K mole V₄O₇ reported elsewhere. The $\Delta S=22.0$ J/K mole V₄O₇ value resulted from the drawing of the baseline as close as possible to the portions of the heat-capacity curve immediately below and above the anomaly. The ΔS value cited in Ref. 5 was obtained in differential scanning calorimeter (DSC) measurements which were taken under nonequilibrium conditions; no details are provided in Ref. 13 concerning the measurement technique. Additionally, great care was exercised in the preparation of the single crystals in the current series of measurements. Also, the small crystallite size and sample mass

TABLE I. Entropy and enthalpy of transition at $T_{MI}=237$ K for V₄O₇.

	Entropy of transition (J/K mole V ₄ O ₇)	Enthalpy of transition (J/mole V ₄ O ₇)
(a) Observed total	22.0	4428
(b) Portion attributed to V ⁴⁺ pairing	13.8	2607
(c) Remaining portion	8.2	1821

used in these measurements ensures uniformity in specimen composition; this is much more difficult to achieve in larger samples. It should be recognized that differences in sample preparation techniques frequently lead to significant discrepancies in ΔS values at the transition. For these reasons the transition entropy cited above differs from the earlier measurements in the literature.

DISCUSSION

Extensive structural studies by x-ray diffraction techniques have been carried out both above and below the metal-insulator transition in V_4O_7 .³¹⁻³⁶ Of particular importance to the present investigation are the findings, based on structural information,^{31,35,36} that even in the metallic state there is considerable charge differentiation among the cations: adjacent strings of V atoms parallel to the pseudorutile c axis in V_4O_7 consist of V^{3+} and V^{4+} units, as shown schematically in Fig. 1. The charge differentiation is incomplete for $T > T_{MI}$ but increases abruptly at the MI transition, and then remains fixed at lower temperatures. A second feature of interest is depicted schematically in Fig. 1(a): At the MI transition the V^{3+} ions pair off into two units, and the interior ions of the V^{4+} string pair off as well. This regrouping becomes increasingly pronounced as the temperature is lowered.³¹

Nuclear magnetic resonance experiments,^{21,22,24} as well as a considerable reduction of the magnetic susceptibility relative to the value anticipated for an equimolar V^{3+} - V^{4+} mixture in V_4O_7 ,^{9,17} have provided additional indirect evidence for cationic pairing below the $M-I$ transition.

Since partial charge localization is common to both the metallic and the insulating phase, we are led to the concept that the insulating phase is stabilized largely through the pair formation process.

Gossard *et al.*²¹ have used NMR measurements as a basis for obtaining more information about spin susceptibilities and the pair-exchange energy J .³⁷ From their Knight shift data between 150 and 240 K they concluded that the V^{4+} pair-exchange energy obeyed approximately the following relation:

$$J/k = 100 + J_0(1 - T/T_{MI})^{1/2}/k, \\ J_0 = 565 \text{ K}, \quad T_{MI} = 237 \text{ K}, \quad (1)$$

where the parameter J_0 is determined by extrapolation of the known temperature dependence of J to 0 K, and T_{MI} is the transition temperature. The specific heat associated with this singlet-triplet spin system can thus be calculated in the mean-field approximation. Above 20 K, $g\mu_B H/kT \ll 1$, and the mean-field contribution to the specific heat becomes negligible. From the partition function, we specify the average energy, $\langle E \rangle$, and the specific heat, $(d\langle E \rangle/dT) \equiv C_J$, by

$$\langle E \rangle = \frac{J(3e^{-x} - 1)}{(3e^{-x} + 1)}, \quad (2)$$

$$C_J = \left[\frac{dJ}{dT} \right] \frac{(3e^{-x} - 1) 6x \exp(-x) [kx/2 - dJ/dT]}{(3e^{-x} + 1)(3e^{-x} + 1)}, \quad (3)$$

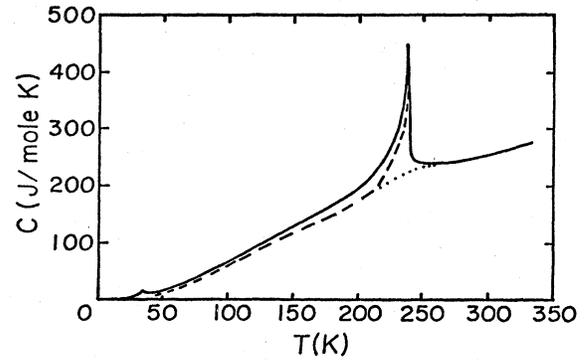


FIG. 4. The specific heat of V_4O_7 before (solid line) and after (dashed line) subtraction of the V^{4+} pair contribution $C_J/2$ determined according to Eq. (3). The dotted line represents the curve used to compute the enthalpy of transition.

where

$$x \equiv \frac{2J(T)}{kT}. \quad (4)$$

Equations (3) and (4) provide an estimate of the heat capacity associated with the variation in V^{4+} - V^{4+} exchange coupling. The results are displayed in Figs. 4 and 5 and in Table I; as is apparent, the above coupling accounts for a significant fraction of the observed heat of transition, thus suggesting a new mechanism for the metal-insulator transition in V_4O_7 . Below 15 K the calculated contribution due to C_J becomes larger than the experimentally observed specific heat, a situation that is clearly unphysical. It was already mentioned by Gossard *et al.*²¹ that the V^{4+} - V^{4+} pairing appears to be complete near 150 K; in this event J becomes constant below 150 K and the use of Eq. (1) below that temperature is unwarranted.

The remaining entropy of transition might be attributed in part to the V^{3+} pair-exchange energy which we have so far ignored. The structural studies demonstrate that the V^{3+} pair distances are not so small as the V^{4+} pair distances, which would point to a reduced pair-exchange energy. On the other hand, the V^{3+} pairs are twice as numerous. Furthermore, they are of spin 1 instead of spin

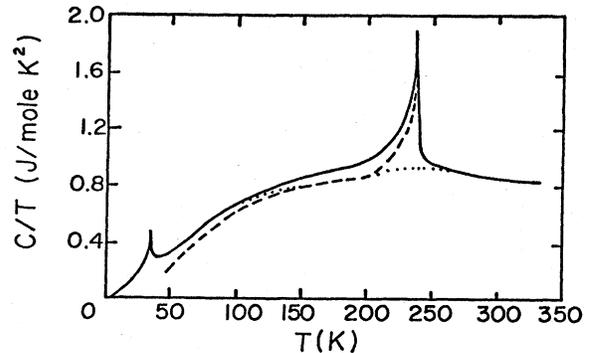


FIG. 5. The specific heat divided by temperature before (solid line) and after (dashed line) subtraction of the V^{4+} pair-exchange contribution $C_J/2$ determined according to Eq. (3). The dotted line represents the curve used to compute the entropy of transition.

$\frac{1}{2}$, so that the $S_i \cdot S_j$ part of the exchange term is four times larger than for the V^{4+} pairs. These arguments suggest that the V^{3+} pair-exchange energy may contribute significantly to the heat of transition. Since the total contribution consists of the product of the number density, the spin term, and the unknown exchange energy, it is not possible to estimate this contribution quantitatively.

In connection with the above it is instructive to model the effect of different types of chain order on the exchange energy. We consider a ring of $2N$ equally spaced ions, of which N are in a 3^+ state of spin $S=1$ and N , in a 4^+ state of spin $S=\frac{1}{2}$. This one-dimensional system should mimic V_4O_7 , because the exchange interaction is exceptionally strong along the rutile c axis, where the V-V distances are shortest. Two limiting cases will be considered: A , the homogeneously mixed case with spins $S=1$ and $S=\frac{1}{2}$ alternating between adjacent sites

$$A: \cdots \frac{1}{2} 1 \frac{1}{2} 1 \frac{1}{2} 1 \cdots,$$

and B , the complete differentiation into a segment of N consecutive units of spin $S=1$, followed by N consecutive units of spin $S=\frac{1}{2}$:

$$B: \cdots 1 1 1 \frac{1}{2} \frac{1}{2} \frac{1}{2} \cdots.$$

The exchange integrals can assume the values $J_{S_i S_j}$ given by J_{11} , $J_{1(1/2)}=J_{(1/2)1}$, and $J_{(1/2)(1/2)}$ for nearest-neighbor (NN) interactions involving the spin types enumerated in the subscripts; interactions beyond NN's are ignored, as are all superexchange effects. The total exchange energy

$$E_J = - \sum_{i>j=1}^{2N} 2J_{ij} S_i \cdot S_j$$

for the antiparallel spins in configuration A is then given by

$$E_{JA} = \sum_{i=1}^{2N} J_{(1/2)1} = 2NJ_{(1/2)1}, \quad (5)$$

while the corresponding quantity for antiparallel spins in configuration B is given by

$$E_{JB} = \sum_{i=1}^N J_{11} + \sum_{i=1}^N J_{(1/2)(1/2)}, \quad (6)$$

where effects due to breaks in the strings $\cdots 111$ and $\frac{1}{2} \frac{1}{2} \frac{1}{2} \cdots$ have been neglected.

Since the radial portions of the wave functions fall off much more rapidly for a 4^+ as compared to a 3^+ ion, it is evident that $|J_{11}| > |J_{(1/2)1}| > |J_{(1/2)(1/2)}|$; thus with $J < 0$, configuration B lies well below A in configuration energy. Furthermore, the configurational entropy of arrangement B is greater than that of A because the breaks between the string of units with $S=1$ and $S=\frac{1}{2}$ can occur in any of the $2N$ positions in the ring. These arguments provide some insight into the experimental fact that charge is localized into a chain of like ions in the insulating and, to some extent, the metallic state of V_4O_7 . This brings into focus the importance of the previously neglected exchange energy. When the exchange energies become sufficiently strong at lower temperatures, pairing

can set it, along the pattern of Fig. 1.

If these views are correct, then it is not necessary to ascribe a large contribution to ΔS from the delocalization of charge carriers, as has been suggested for Ti_4O_7 ,³⁸ for example. Consequently, the electronic specific heat in the metallic state, γ , could then be either small at all temperatures (mobile carriers in a wide band), or large only at low temperatures (Fermi level, ϵ_f , is near the upper band edge of a narrow band).

A portion of the transition entropy might be ascribed to the charge differentiation process itself as has been suggested by Terukov *et al.* for V_3O_5 ,³⁹ or to charge delocalization effects. It is postulated by Kopaev *et al.*^{40,41} that charge carriers tend to be trapped near the V_2O_3 -like sites at the shear planes, and that the delocalization takes place at the metal-insulator transition. However, it is clear that the exchange energy contributes a very significant portion to the heat of transition.

If, as suggested by the above evidence, the transition from metal to insulator is driven principally by exchange-coupled cation pairing, then this mechanism is similar to that discussed by Peierls.⁴² In his spinless model for pairing, however, a gap opens due to the difference in energy between pair bonding and antibonding bands, with ϵ_f located in the resultant gap. In our case, a gap equal to the pair-exchange coupling is thought to separate the spin singlet and triplet pair states. Since the singlet and triplet states are both two-electron states, ϵ_f may, but need not, lie between the two. This immediately raises the question of what gives rise to the metallic state. One possibility is that in the metallic state, the lower band edge of a much wider band overlaps with one of the very narrow singlet pair states. With decreasing temperature the intrapair distance decreases; the singlet states are consequently lowered in energy. Ultimately, the narrow and wide bands become separated in energy, thus producing an energy gap ϵ_g and the insulating state. If this is the case, ϵ_g should satisfy the criterion $\epsilon_g \leq 2J(T)$, where $J(T)$ is the exchange coupling for appropriate pair. This mechanism is shown schematically in Fig. 6. From the specific

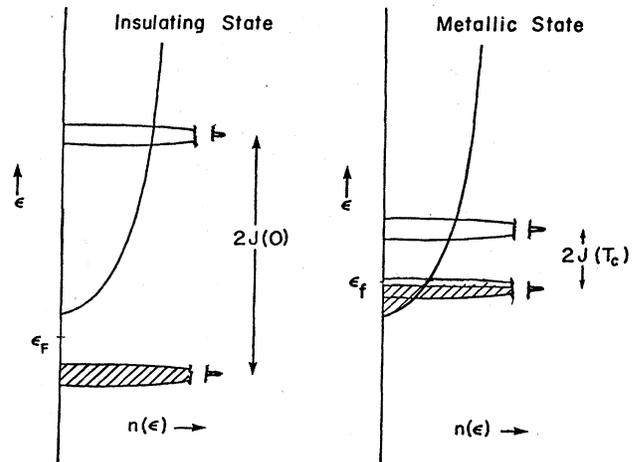


FIG. 6. A proposed density of states as a function of energy for both the insulating and metallic phases of V_4O_7 .

heat measurements we had earlier concluded that $J(T)$ for the V^{4+} pair should be nearly constant below about 150 K. This model would therefore predict a band gap of about 0.1 eV or less between 0–100 K which then collapses with increasing temperature as T approaches T_{MI} . A search for the optical edge in infrared transmission could test this hypothesis.

The above analysis does not rule out the possibility that electron delocalization also contributes to the entropy change at the transition; however, any significant contribution would require that the itinerant electrons move in a very narrow band. Even then, exchange coupling would provide much of the driving force for the transition.

The specific heat measurements presented here, taken with previous results, present the possibility that pair-exchange coupling in V_4O_7 drives the transition from the metallic to the insulating state. Furthermore, they imply that the metallic state may be characterized by the coexistence of d electrons in essentially localized and itinerant states, in the manner shown in Fig. 6. This picture has much in common with evidence adduced for other Magnéli compounds concerning the occurrence of these two types of d electrons.⁴³

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*Permanent address: Research and Development Center, General Electric Company, Schenectady, NY 12309.

†Present address: IBM Thomas J. Watson Research Center, Yorktown Heights, NY 10598.

‡Permanent address: Aircraft Engine Group, General Electric Company, Cincinnati, OH 45215.

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