

Microscopic magnetic properties of metallic and insulating V_4O_7 and V_7O_{13}

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The local magnetic properties of the various atomic sites in metallic and insulating V_4O_7 and V_7O_{13} have been determined by means of ^{51}V nuclear magnetic resonance. Remarkably free-spin-like paramagnetic behavior is found in metallic V_4O_7 and V_7O_{13} , although there is not full differentiation into 3+ and 4+ charge states on the different sites. Below the V_4O_7 metal-insulator transition, one group of V^{4+} ions forms nonmagnetic singlet spin pairs in the insulating phase while the remainder of the sites are paramagnetic. In the antiferromagnetic insulating state two magnetic vanadium sites with hyperfine fields 70.1 and 78.4 kOe and one nonmagnetic vanadium site are found. These results are analyzed in terms of various theoretical models, i.e., a modified Hubbard model and small-polaron model. None of the theoretical models is satisfactory.

I. INTRODUCTION

In addition to VO_2 and V_2O_3 , there are a number of other vanadium oxide compounds of intermediate composition which also show well-defined metal-insulator transitions.^{1,2} A series of these compounds, known as the Magnéli-phase compounds, are structurally related and have compositions $V_2O_3 + (n-2)VO_2 = V_nO_{2n-1}$. The oxygens form a slightly distorted close-packed hexagonal lattice, and the vanadium atoms are octahedrally oxygen coordinated. These Magnéli compounds form a homologous series where only the arrangement of the V atoms in the oxygen lattice varies across the series. Here we discuss work on two such compounds, V_4O_7 and V_7O_{13} . V_4O_7 has a 250 °K metal-insulator transition while V_7O_{13} is metallic at all temperatures.

These compounds, unlike VO_2 and V_2O_3 , have mixed valences and can have a nonuniform distribution of charge among the atomic cells or nonintegral charge occupations of the cells. Because of the mixed 3+ and 4+ vanadium valences, the factors affecting their metal-insulator transitions are expected to be quite different than for VO_2 and V_2O_3 . In particular, charge transfer between sites of different valence is not inhibited by Coulomb intra-atomic interactions, in contrast to the single-valence materials. The intra-atomic Coulomb energy cannot by itself stabilize the insulating state, leaving *interatomic* Coulomb interactions, especially V-O interactions, a more important source for differentiating metallic and insulating state energies. Understanding of these effects will be aided by any measurements which succeed in identifying local distributions of spin and charge. V^{3+} sites will have $3d^2$ electronic configurations, while V^{4+} sites will have $3d^1$. In the absence of orbital effects, such sites should show $S=1$ and $S=\frac{1}{2}$ spin behavior,

respectively, allowing for the possibility of determining the charge distributions magnetically.

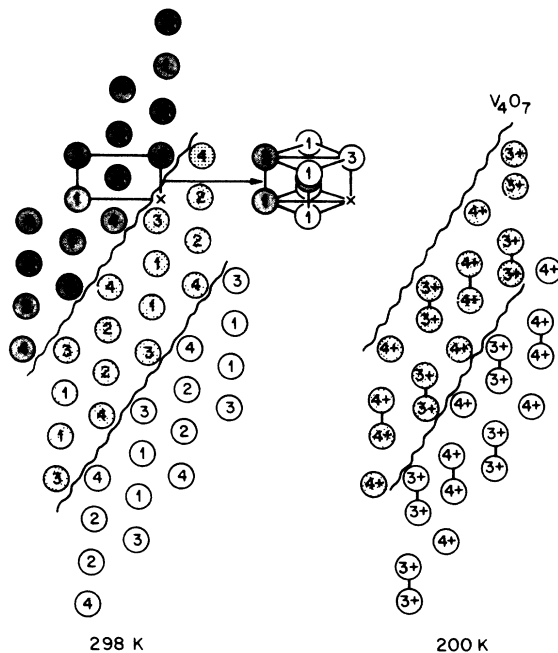
In this paper, we report a study of the microscopic magnetic properties of V_4O_7 and V_7O_{13} by means of nuclear-magnetic-resonance techniques. Nuclear magnetic resonance offers an attractive way to investigate the microscopic properties since the response of inequivalent sites can, in principle, be resolved in the nuclear-resonance spectra, and since the variations in local behavior which might be expected, such as paramagnetic local moments, band paramagnetism, singlet spin pairs, and antiferromagnetism, all have quite characteristic signatures in nuclear-resonance experiments.

The crystal structure and the bulk magnetic susceptibility of the phases have been investigated previously. The most complete descriptions of the crystal structure are available for V_4O_7 ³ and V_5O_9 ,⁴ where single crystals have been available, and structures both above and below the transition temperature have been determined. In V_4O_7 , four inequivalent vanadium sites (Fig. 1) were found. The valences of the sites were estimated from vanadium-oxygen distances and showed a markedly increased differentiation in the insulating phase. Pairing also occurred between three of the four types of sites in the insulating phase. In Fig. 2, the bulk susceptibility data of Ref. 2 are shown for VO_2 , V_2O_3 , V_4O_7 , and V_7O_{13} . V_4O_7 is metallic above 250 °K and insulating below. It was suggested that the peak in the susceptibility at 40 °K corresponds to an antiferromagnetic transition.¹ V_7O_{13} , on the other hand, is metallic at all temperatures, its susceptibility peak at 50 °K apparently also corresponding to antiferromagnetic ordering.¹

In both V_4O_7 and V_7O_{13} , the metallic-state susceptibility is larger and more temperature dependent than for VO_2 and V_2O_3 . Kosuge² fitted the metallic-state data for V_4O_7 in the small temperature

range observed above the 250 °K transition to a Curie-Weiss form $\chi_m = 0.60/[T + (20 \pm 5)]$. The Curie constant is nearly the value (0.67) expected for an equal division between $S = \frac{1}{2}$ and $S = 1$ local moments.

Equal numbers of the two types of moments are expected from the composition $V_4O_7 (= V_2O_3 + 2VO_2)$, which results in two nominal V^{3+} ions and two V^{4+} ions per formula unit. However, the close resemblance to purely local-moment behavior with well-differentiated $3+$ ($S = 1$) and $4+$ ($S = \frac{1}{2}$) sites suggested by this result is surprising in view of (i) the metallic properties of the phase and (ii) the relatively small differences in vanadium-oxygen distances among the four inequivalent sites in metallic V_4O_7 . The reduced susceptibility in the insulating phase of V_4O_7 has been attributed to singlet



AVERAGE METAL OXYGEN DISTANCE Å
EACH OCTAHEDRON

ATOM	298 K	200 K	PREDICTED
1	1.967 (2)	1.948 (2)	1.94 V^{4+}
2	1.980 (2)	1.992 (2)	2.01 V^{3+}
3	1.969 (2)	1.961 (2)	1.94 V^{4+}
4	1.984 (2)	2.009 (2)	2.01 V^{3+}

FIG. 1. Structure diagram from Ref. 20 for V_4O_7 in metallic phase (298 °K) and insulating phase (200 °K). The diagram shows the pattern of charge localization (+3, +4) and pairing of vanadium ions (heavy lines) in the insulating phase and the undistorted structure of the metallic phase. The numbers in the center figure designate the crystallographically inequivalent sites.

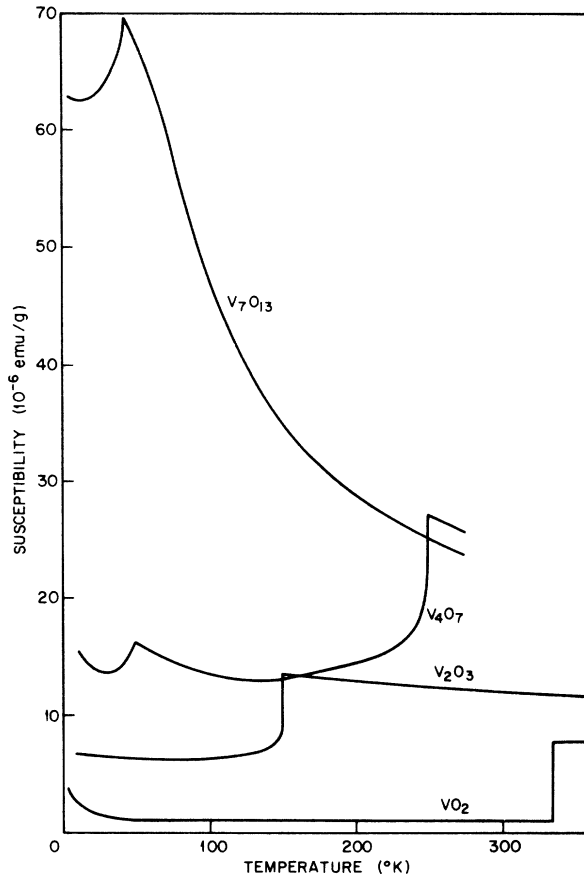


FIG. 2. Magnetic susceptibilities of V_7O_{13} and V_4O_7 (from Ref. 2), V_2O_3 (from Ref. 5), and VO_2 (from Ref. 8).

spin pairing of $V^{3+}-V^{3+}$ and $V^{4+}-V^{4+}$ ions. This is also surprising in view of the ultimate antiferromagnetic ordering below 40 °K, which would require localized moments rather than singlet spin pairs. Crystallographic studies have shown *structural* pairing involving three quarters of the atomic sites, the remaining quarter of the sites remaining unpaired. For V_7O_{13} also, the susceptibility was fitted to a Curie-Weiss law, with a resultant $\theta = -38$ °K and $C = 0.53$, close to the value $C = 0.55$ calculated for two V^{3+} and five V^{4+} ions per formula unit. This is again surprising in view of the metallic nature of V_7O_{13} .

Our nuclear-magnetic-resonance measurements reveal magnetically inequivalent sites in the metallic phase of V_4O_7 and V_7O_{13} , with evidence that the sites are not fully differentiated into localized-spin $S = \frac{1}{2}$ and $S = 1$ states. We shall also show evidence for simultaneous existence of spin-paired and local-moment sites in the insulating phase of V_4O_7 both above and below the magnetic ordering temperature.

The measurements reported here, taken together

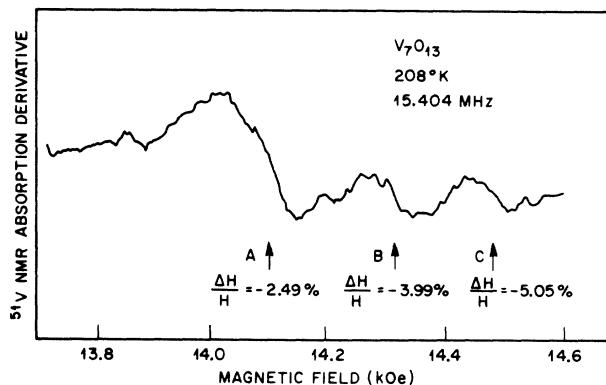


FIG. 3. ^{51}V nuclear-magnetic-resonance absorption derivative of V_7O_{13} at 208°K. The operating frequency is 15.404 MHz and the frequency shifts $\Delta H/H$ are quoted with respect to a sodium vanadate reference solution.

with the earlier work, pose some interesting theoretical questions. It appears that a Hubbard model, or a simple extension thereof, is inadequate to explain the data. In particular, the marked contrast between the magnetic properties of these mixed-valence Magnéli phases and the single-valence compounds VO_2 and V_2O_3 is difficult to understand. Since metallic behavior is tied to existence of charge or valence fluctuations, it is a surprise that mixed-valence materials should be so much more localized than their single-valence counterparts. This and related questions are covered in Sec. IV.

II. EXPERIMENTAL

The polycrystalline V_4O_7 sample was prepared by heating a stoichiometric mixture of V_2O_3 and VO_2 powder of ~ 5 ppm cation impurity content in an evacuated quartz tube at 800°K for 16 h and subsequently at 1000°K for 5 h. The composition and structure were confirmed by powder x-ray diffraction. The V_7O_{13} sample was prepared in Kyoto by reaction of V_2O_3 and V_2O_5 as described in Ref. 1 and the structure was also confirmed by x rays.

Nuclear-resonance measurements were made with a Varian Associates wide-line NMR spectrometer and associated signal-averaging equipment for cw measurements in the 16-MHz range and with a coherent pulsed spectrometer for observation of spin-echo spectra and nuclear-relaxation times in the 50-MHz range. Frequency shifts were measured relative to NaVO_3 and HF reference solutions.

A. V_7O_{13}

Three ^{51}V nuclear resonance lines, denoted A, B, and C, could be resolved in metallic V_7O_{13} in the temperature range 77 to 300°K. A typical nuclear

absorption derivative spectrum is shown in Fig. 3. The peak-to-peak linewidths of the components are 130, 80, and 80 Oe at 208°K. The line positions were temperature dependent, as shown in Fig. 4. With changing temperature, the linewidths increased proportionally to the frequency shifts reaching 340, 225, and 175 Oe at 77°K. No cw lines could be detected at 4.2 or 20°K, in confirmation of the previously deduced low-temperature antiferromagnetism of the material. Pulsed measurements were not made on V_7O_{13} .

The temperature dependence of the metallic-state frequency shifts will be used below to estimate the degree of localized magnetic behavior. The effective valences of the different sites in V_7O_{13} will also be estimated.

B. V_4O_7

In the metallic phase of V_4O_7 , three negatively shifted nuclear-resonance lines, also denoted A, B, and C, were also resolved at temperatures between 250 and 410°K. The frequency shifts were temperature dependent, with the shifts vs temperature being displayed in Fig. 5. The more negatively shifted (C) line's width (peak to peak of the absorption derivative) was 50 Oe, while the less-shifted lines were incompletely resolved, having widths ~ 80 Oe. In the V_4O_7 insulating phase, however, only a single line was observed, having a linewidth varying from 56 Oe at 77°K to 48 Oe at 210°K, and increasing to 100 Oe just below the transition to the metallic state. At 20 and 4.2°K, where the sample is reported to be antiferromagnetic, no signal is observable with the cw NMR spectrometer. With a pulsed spectrometer, however, several ^{51}V nuclear spin echoes were observable at 4.2°K. A double-peaked spectrum of spin-echo amplitude vs field, 3400 Oe in width, as

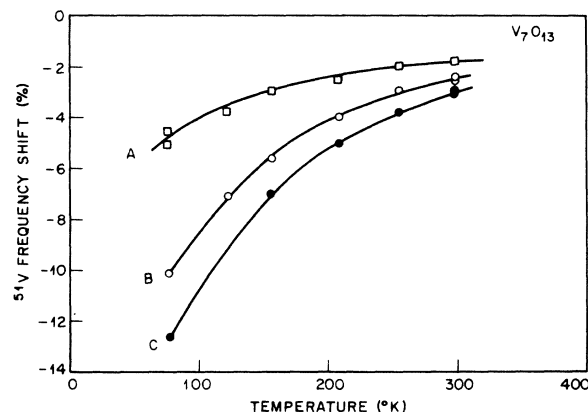


FIG. 4. Temperature dependence of ^{51}V frequency shifts in V_7O_{13} . A, B, and C refer to corresponding points in Fig. 3.

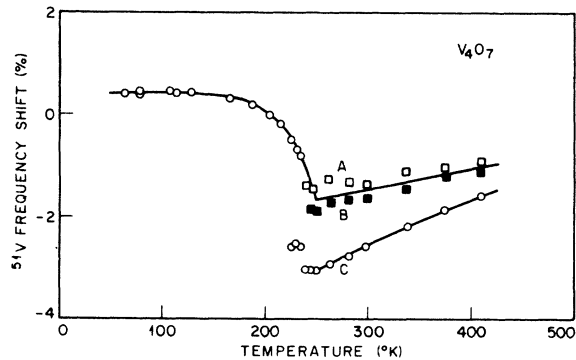


FIG. 5. Temperature dependence of ^{51}V frequency shifts in V_4O_7 .

seen in Figs. 6(a) and 6(b) was found centered at the same frequency shift (+0.4%) as the 77°K insulating-state cw line. We shall show below that it arises from nonmagnetic singlet spin-paired vanadium sites experiencing an internal field of 1740 Oe from interaction with atoms having moments. The breadth of the line accounts for its absence in the cw measurements. In addition, nu-

clear spin echoes were observed at 4.2°K at two lower fields with the asymmetric spectra of spin-echo amplitude vs field seen in Fig. 6(c). The fields for maximum echo response *decreased* with increasing frequency, with a slope corresponding to the ^{51}V gyromagnetic ratio. We associate these responses with magnetized moment-bearing vanadium sites with internal fields of 70.1 and 78.4 kOe. The observability of all these lines with pulse techniques is due to the frequency breadth of the 3- and 2- μsec transmitter pulses and to the possibility of echo detection without field or frequency modulation. At 77°K a single quadrupole-broadened echo spectrum centered at $K=+0.4\%$ with $\nu_Q=0.62$ MHz was observed. No echoes could be observed in the metallic state of V_4O_7 above 250°K, however, We attribute this to an increased relaxation rate in the metallic phase. The spin-echo decay time T_2 , measured at 77°K in the insulating state, is $(6.2 \pm 1.0) \times 10^{-5}$ sec, and the recovery time T_1 from a train of saturating pulses is $(4.1 \pm 0.8) \times 10^{-3}$ sec, also at 77°K. At 4.2°K,

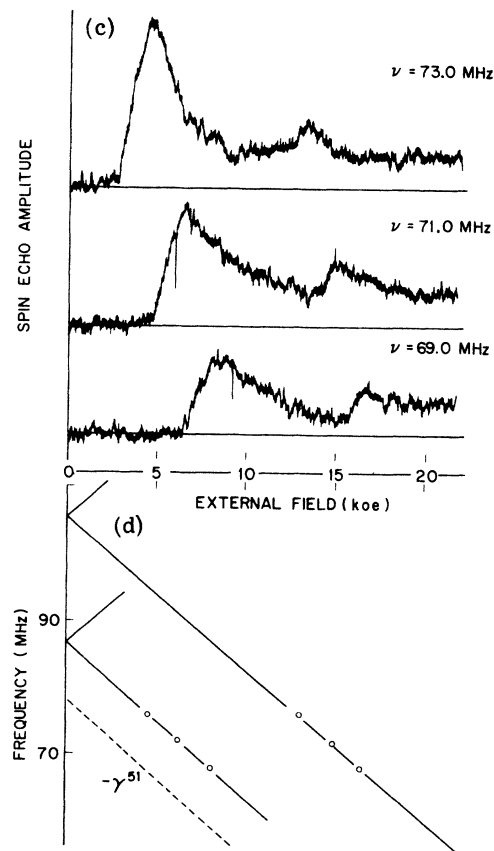
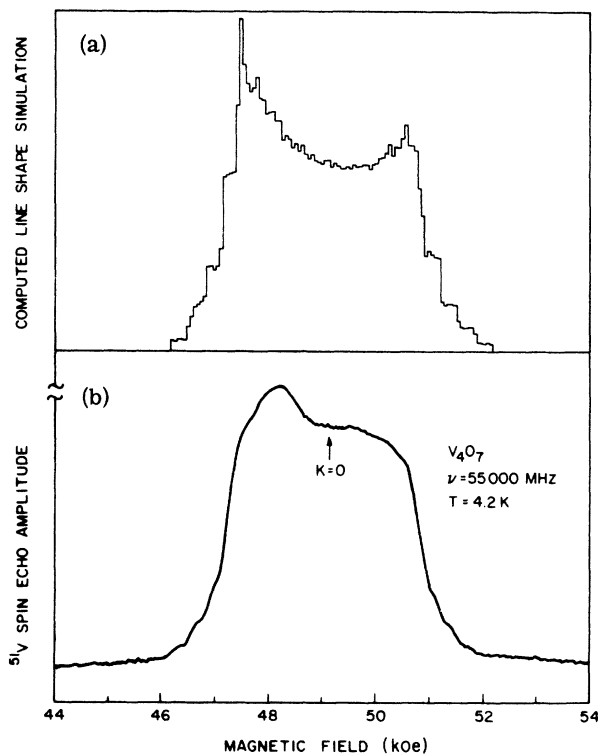


FIG. 6. Spin-echo amplitude of ^{51}V in insulating antiferromagnetic V_4O_7 at 4.2°K as a function of externally applied magnetic field. (a) Computer-generated powder line shape with $\nu_Q=0.62$ MHz, $H_{\text{int}}=1.74$ kOe, $K_{\parallel}-K_{\perp}=-0.55\%$, $\eta=0$. (b) Observed spectrum at high applied field. (c) Observed spectra at lower applied field. (d) Frequency vs field for spin echo maxima.

$T_2 = (1.8 \pm 0.2) \times 10^{-4}$ sec and $T_1 = (1.0 \pm 0.2) \times 10^{-1}$ sec.

III. ANALYSIS

In those vanadium oxide compounds studied previously by nuclear resonance, the primary sources of magnetic susceptibility, and thus internal magnetic field and frequency shift of the nuclei, were the $3d$ spin paramagnetism and the $3d$ orbital field-induced Van Vleck paramagnetism.⁵⁻⁷ The $4s$ orbitals of the vanadium ions are essentially unoccupied and do not produce a susceptibility contribution. This should also be true for V_4O_7 and V_7O_{13} .

In the antiferromagnetic state of the materials, static $3d$ spin hyperfine fields of the order of 10^5 Oe are expected on sites with moments. In the paramagnetic regimes, frequency shifts from spin and orbital paramagnetism are in the percent range, allowing observation of resonances and measurement of shifts. The predominant source of temperature dependence of shifts and susceptibilities in this regime is the spin paramagnetism, since the orbital paramagnetism is primarily a field-induced Van Vleck temperature-independent paramagnetism, involving states spread over energy ranges much greater than kT .

Considering first V_7O_{13} , where the observed paramagnetic susceptibilities reach the highest values in the series of Magnéli phases and where the sample is metallic at all temperatures, the observation of three nuclear resonances shows that all sites are not magnetically equivalent. The spin susceptibility of each site χ_{spin} may be determined from its nuclear-resonance frequency shift by first subtracting the orbital component K_{orb} from the observed shift K_{total} and then dividing the resulting spin component of the frequency shift K_{spin} by the spin hyperfine coupling constant H_{spin}^{hf} . Thus

$$\chi_{spin} = \frac{K_{spin}}{A \mu_B H_{spin}^{hf}} = \frac{K_{total} - K_{orb}}{A \mu_B H_{spin}^{hf}}.$$

A is Avogadro's number and χ_{spin} is per mole of V atoms. Previous measurements on both vanadium fluorides and oxides have shown that K_{orb} and H_{spin}^{hf} depend on valence. From VO_2 we obtain, for V^{4+} in the octahedral oxygen coordination appropriate here, $K_{orb} = +0.28\%$ (temperature-independent Van Vleck paramagnetism) and $H_{spin}^{hf} = -85$ kOe/μ_B .^{7,8} From V_2O_3 , we find, for V^{3+} in octahedral oxygen environment, $K_{orb} = +1.23\%$ and $H_{spin}^{hf} = -120$ kOe/μ_B .⁵ Orbital contributions to the local moment are apparently quenched. In order to extract local spin susceptibilities, we try as a first approximation V^{3+} values of H_{spin}^{hf} and K_{orb} for the two more negatively shifted NMR lines and V^{4+} values for the less-shifted line. Values of local

$1/\chi_{spin}$ vs T which are so determined are shown in Fig. 7(a). Also shown for comparison are Curie-Weiss values of $1/\chi_{spin}$ for $S = \frac{1}{2}$ and $S = 1$ with the common Weiss $\theta = -38^\circ K$ proposed in Ref. 2. $1/\chi_{spin}^{total}$ determined from the NMR is shown in Fig. 7(b) and is in substantial agreement with $1/(\chi_{meas} - \chi_{orb})$, but the agreement between the individual site susceptibilities and those predicted for complete $3+$ and $4+$ site differentiation is quite poor. The observed slopes of local $1/\chi_{spin}$ give $p_{eff} = 2.16$ and 2.06 , which differ by much less than the factor $\sqrt{\frac{8}{3}}$ expected for $S = 1$ and $S = \frac{1}{2}$. This

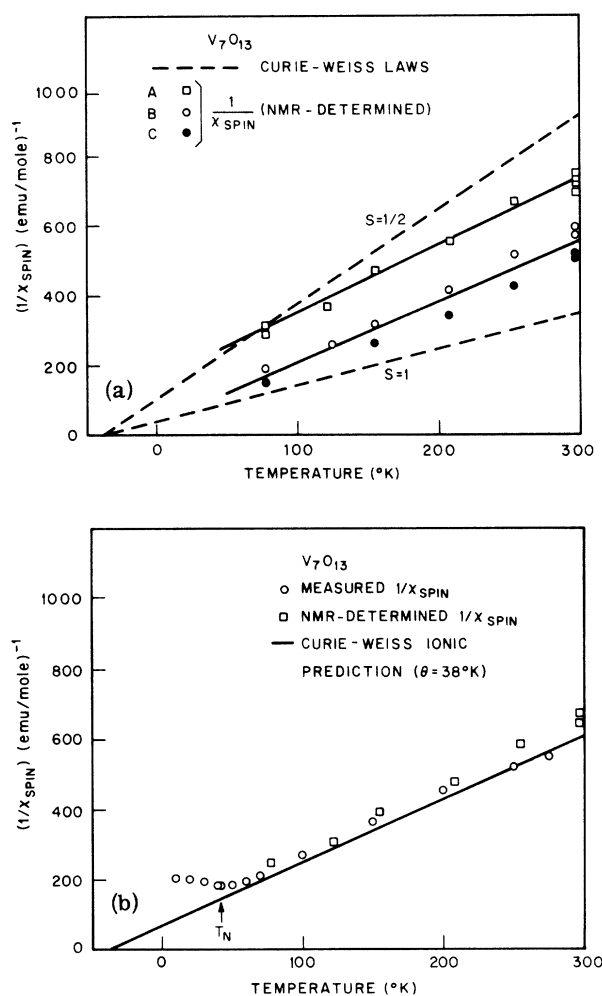


FIG. 7. (a) Local inverse magnetic susceptibilities of sites A, B, and C in V_7O_{13} as determined from nuclear-resonance frequency shifts. Orbital frequency-shift values and spin hyperfine coupling constants used are quoted in text. $4+$ values were used in deriving \square points and $3+$ values for \bullet and \circ points. Dashed lines show Curie-Weiss predictions for $S = \frac{1}{2}$ and $S = 1$ with $\theta = -38^\circ K$. (b) Comparison of total measured NMR-determined and Curie-Weiss-predicted total inverse susceptibilities for sum of all sites.

suggests little charge differentiation with most of the susceptibility difference due to differences in Weiss θ . Since the degree of charge differentiation, and thus moment differentiation, might be temperature dependent, however, quantitative fits are subject to error. Should the 3+–4+ admixtures be temperature dependent with both sites having equal θ 's, we estimate d -electron site occupancies of 1.86 d electrons and 1.14 d electrons for the more and less magnetic sites at 77 °K, and 1.67 and 1.33 d electrons for the two types of sites at 300 °K. In no case is complete differentiation into sites with one and two d -electron occupancy found, however. This is consonant with expectations for a metallic material.

The fact that nuclear resonances are resolved from the inequivalent sites in V_7O_{13} deserves comment and allows us to place limits of some of the fluctuation rates of the spins on the observed sites. Exchange between the vanadium spins produces mutual spin flips which, in turn, produce a nuclear relaxation rate⁹

$$\frac{1}{T_1} = \frac{1}{T_2} = \frac{(2\pi)^{1/2} A^2 S(S+1)}{3\hbar^2 \omega_{\text{ex}}} \sim 3 \times 10^5 \text{ sec}^{-1}$$

for $A/\hbar = 7 \times 10^8 \text{ sec}^{-1}$, $S=1$, and

$$\omega_{\text{ex}} = \frac{J[zS(S+1)]^{1/2}}{\hbar} \approx \frac{3kTc}{2\hbar[zS(S+1)]^{1/2}} \approx 3 \times 10^{12} \text{ sec}^{-1}.$$

The linewidth associated with this relaxation rate is ~ 100 kHz, or ~ 100 Oe, which is close to the observed widths. In addition to this fluctuation there will also be charge fluctuations. As a site fluctuates from single to double d -electron occupancy, a fluctuation from a spin $S = \frac{1}{2}$ to $S = 1$ on that site will occur. Since the nuclear-resonance frequency during the $S = 1$ occupancy may be $\sim 10\%$ less than during $S = \frac{1}{2}$ periods, this is a potential broadening mechanism. Such fluctuations must occur in V_7O_{13} in order to produce the frequency shifts which are intermediate between $S = \frac{1}{2}$ and $S = 1$ behavior. The observed lines are apparently being narrowed by motional averaging effects. The condition that a $\Delta\nu = 1.6$ -MHz splitting be narrowed to the observed $\delta\nu = 0.1$ -MHz linewidths is that the fluctuation frequency ν_{fluc} between site occupancy states be

$$\nu_{\text{fluc}} \geq \frac{(\Delta\nu)^2}{\delta\nu} = 3 \times 10^7 \text{ sec}^{-1}.$$

Such a fluctuation frequency, being only $\sim 10^7$ eV is easily achieved by typical intersite transfer integrals between inequivalent sites in a metal.

In V_4O_7 , a similar analysis may be used to determine the local spin susceptibilities from the ob-

served nuclear-resonance frequency shifts. In this case, three lines are again resolved. The temperature range over which the metallic state exists is more limited because of the 250 °K metal-insulator transition. The same parameters are used for orbital shift and spin hyperfine coupling constants with the exception that $K_{\text{orb}}^{4+} = +0.4\%$ is used, as determined below from insulating state measurements in V_4O_7 . In Fig. 8 a Curie-Weiss plot of the deduced spin susceptibilities is shown under assumption of 3+ and 4+ parameters for the more magnetic singlet and less magnetic doublet. Again, much less differentiation in Curie constant is seen than the expected factor 2.67 for $S = \frac{1}{2}$ and $S = 1$. We conclude that we are again in a fluctuating regime in which the sites are inequivalent, but are each occupied fractionally both by V^{3+} ($3d^2$) and V^{4+} ($3d^1$). Again, the fact that the slopes of the Curie-Weiss fits are so similar may be caused by a changing charge distribution with temperature, with the sites being more nearly equivalent at high temperatures. Under the assumption that all sites have equal Weiss θ 's, one estimates d -electron site occupancies of 1.67 and 1.33 for the two sites at 410 °K, and 1.75 and 1.25 for the two types of site at 250 °K. The less-shifted sites (A and B) with the smaller average spin and d -electron occupancy could be assigned to the crystallographic sites (1) and (3) of Fig. 1 on the basis of their smaller, more 4+-like V-O distances. Assignment to sites (1) and (2) is also possible, however, on the basis of the more nearly rutile-like V-V coordination of these sites in the interior to the shear plane slabs.

The observation of a single line with a frequency shift approaching a constant value of $+0.4\%$ in the insulating state below 250 °K suggests that there we are observing a site with greatly reduced spin magnetization. The x-ray determination of the V_4O_7 crystal structure³ shows both 3+–3+ and 4+–4+ ion pairs in the I state. The 4+ sites would be expected to undergo singlet spin pairing, while the 3+ sites with $S = 1$ might pair in singlet, triplet, or quintuplet spin states. The close proximity of the $+0.4\%$ frequency shift to the $+0.3\%$ Van Vleck orbital shift of V^{4+} ions in VO_2 ⁷ leads us to assign the observed resonance to the 4+–4+ singlet pairs. The 3+ sites and the unpaired 4+ site are not seen in the nuclear resonance, presumably being sufficiently magnetic to broaden the nuclear resonance by short-range order or by rapid magnetic relaxation. Such sites produce the bulk of the I -state susceptibility and the ultimate low-temperature anti-ferromagnetism of V_4O_7 .

The gradual change in susceptibility and frequency shift below the metal-insulator transition and the absence of large discontinuities at the transition indicate that the transition is much less strongly first order in V_4O_7 than in most of the

other vanadium oxides. The 4+–4+ pairing apparently becomes complete only below $\sim 150^\circ\text{K}$. Inhomogeneities cannot be responsible for the width of the transition to a fully paired state since only a single sharp nuclear resonance is observed through most of the transition region. Since the spin susceptibility of exchange-coupled spin pairs is well defined and known at all temperatures, it is possible to use the observed frequency shifts to find the spin susceptibility and thus the exchange coupling $+2J\vec{S}_i \cdot \vec{S}_j$ between spins \vec{S}_i and \vec{S}_j of the 4+–4+ pairs. The expectation value of S_z per atom for $g\mu_B H \ll kT$ is¹⁰

$$\langle S_z \rangle = \frac{g\mu_B H / kT}{e^{2J/kT} + 3}.$$

The values of J so deduced are shown in Fig. 9 and are seen to increase below the transition, with J/k ultimately exceeding 400°K . The metal-state spin susceptibility for the less magnetic sites just above the transition corresponds to an effective J/k of 100°K . It is interesting that $(J-100)$ is proportional to $(T-T_M)^{-1/2}$ and thus may be an order parameter for the transition.

The NMR spectrum of spin-echo amplitudes observed at 4.2°K implies a continued singlet spin pairing in the antiferromagnetic state, with the singlet V^{4+} spin pairs unbroken by the antiferromagnetic ordering of the spins on the remaining sites. The nonmagnetic-site Van Vleck frequency shift is $+0.4\%$, just as in the paramagnetic insulating state, together with a spontaneous internal field of 1740 Oe. The internal field is of the order of that expected for supertransferred hyperfine interactions, rather than the ~ 85 kOe expected for a magnetic site with one Bohr magneton of local moment. The line shape is accounted for by the randomly oriented powder sample, in which the

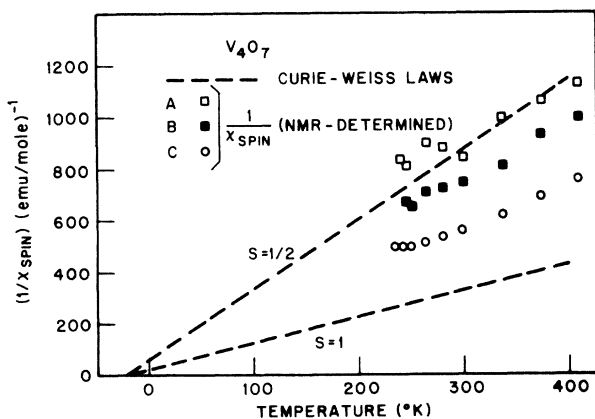


FIG. 8. Local inverse magnetic susceptibilities of V_4O_7 determined from nuclear-resonance frequency shifts for sites A, B, and C.

spin susceptibility and field H_0 are too small to produce an appreciable orientation of spin moments and hyperfine fields H_{int} . Under this circumstance, a basically rectangular spectrum is expected extending from $H_0 + H_{\text{int}}$ to $H_0 - H_{\text{int}}$. Steps associated with first-order quadrupole splittings are observable at the low- and high-field edges of the spectrum. The depression of the center of the line apparently results from quadrupole effects also, with the mean quadrupole splittings for spins in this part of the spectrum being larger and the intensity correspondingly weaker than for the edges of the spectrum. The asymmetry of the line is probably caused by the anisotropic susceptibility of the antiferromagnetic state, which will shift the resonances of spins with hyperfine fields parallel to the applied field less than those with fields perpendicular, i. e., will produce an anisotropic frequency shift. A computer-generated random powder line shape with $\nu_Q = 0.62$ MHz, $\eta = 0$, $H_{\text{int}} = 1.74$ kOe, and a frequency-shift anisotropy $K_{\parallel} - K_{\perp} = -0.55\%$ is shown in Fig. 6(a) and yields good agreement with the observed spectrum in Fig. 6(b).

The spin-echo spectra observed at lower applied fields with extrapolated internal fields of 70.1 and 78.4 kOe obviously arise from sites with magnetic moments. The echo spectra peaks correspond to edges of spectra extending from $H_{\text{int}} - \omega/\gamma$ to $H_{\text{int}} + \omega/\gamma$, the edges observed in this case being those at $H_{\text{int}} - \omega/\gamma$. The internal fields are of the magnitude expected from sites with magnetizations near one Bohr magneton. Two possible assignments of the echo lines to crystallographic sites are possible: (i) One line arises from unpaired 4+ atoms (site 4) with moment of one Bohr magneton, while the other results from paired 3+ atoms (sites 2 and 4) which have reduced moments of one Bohr magneton, owing to covalent singlet bonding of one of their two $3d$ electrons. (ii) Both lines arise from unpaired 4+ atoms, which may have become crystallographically inequivalent in the antiferromagnetic state. The first possibility could be confirmed by measurements, possibly inelastic polarized slow neutron scattering¹¹ showing no sites with hyperfine fields greater than 78.4 kOe, while the second possibility would be indicated by low-temperature crystallographic inequivalence of unpaired V^{4+} sites.

IV. DISCUSSION

The measurements reported here taken together with the earlier transport,² and susceptibility measurements¹ and the crystallographic studies^{3,4} establish the basic properties of the Magnéli phases. The theoretical questions posed by these results are very interesting. They fall into three classes. In the first place, there is the question whether any of the current models can adequately explain

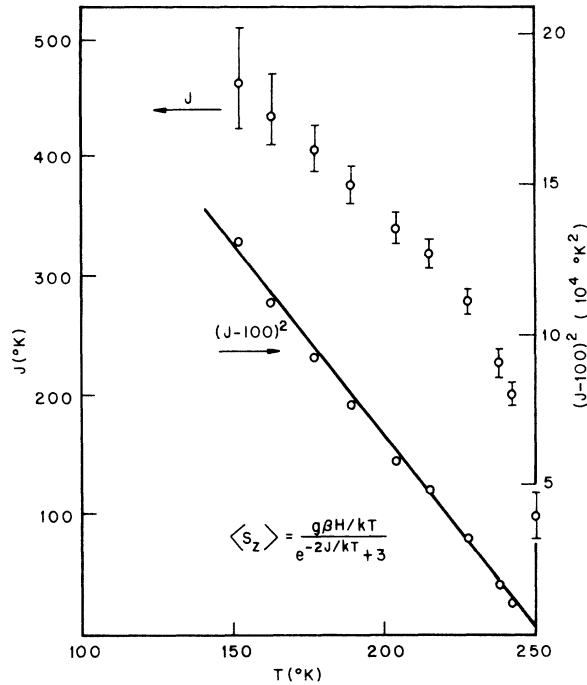


FIG. 9. Exchange J between $V^{4+} S = \frac{1}{2}$ paired spins in insulating V_4O_7 when $H_{ex} = 2J\vec{S}_i \cdot \vec{S}_j$.

the remarkable properties of the metallic phases common to all of these compounds. Secondly, there are the insulating phases and the question of which model is appropriate. Finally, there is the problem of identifying the driving force of the metal-insulator transitions. We shall discuss these questions in order.

It is apparent that the properties of the metallic phases are common to all of the Magnéli phases V_nO_{2n-1} with $n \geq 4$. These metals have unusual magnetic properties. From the magnetic point of view, these metals look like well-localized magnetic insulators with strongly temperature-dependent susceptibilities with weak antiferromagnetic interactions. This of itself is quite remarkable, but it is even more remarkable in comparison to the end members of the series, VO_2 and V_2O_3 . Both these compounds have magnetic susceptibilities which, though clearly exchange enhanced and somewhat temperature dependent, are much smaller and much less temperature dependent. The metallic phases of the mixed-valence compounds behave with regard to their magnetic properties in a much more localized fashion than do the corresponding phases of the single-valence compounds. It should be pointed out, however, that the mixed valence compounds with mixtures of d^0 and d^1 configurations, e. g., V_6O_{13} and Ti_4O_7 have values of the magnetic susceptibility comparable to VO_2 .

The conventional resolution of such a paradox is to ascribe the localized and itinerant behavior to different groups of electrons, as in rare-earth metals. Thus the metallic character might be due to a small group of vanadium $4s$ electrons while the vanadium $3d$ electrons were well localized. The strongest piece of evidence against such a model is the specific-heat measurement of McWhan *et al.*¹² They found a very large linear term in the specific heat of V_7O_{13} , which remains metallic, which corresponds to a density of states of ≈ 14 $eV^{-1}V^{-1}$. Such a large value implies that the V $3d$ band is at the Fermi level. While the recent specific-heat results of Sjöstrand and Keesom¹³ demonstrate that a small number of carriers can cause a large linear specific heat over a limited region, the measurements of McWhan *et al.*¹² show a clear contrast between metallic V_7O_{13} and insulating V_4O_7 and show a specific heat quite different in its temperature dependence in V_7O_{13} than in the $Ti_{2-x}V_xO_3$ series studied by Sjöstrand and Keesom. Since the Knight shift is very sensitive to small amounts of "s" character, it is clear from the results shown in Figs. 4 and 5 that the amount of s character is small. A reasonable upper limit on the fractional s character is that it is ≤ 0.05 . Even if we accept a small admixing of the $4s$ band in the metallic state, it is by no means clear how to reconcile the expected hybridization of $4s$ and $3d$ bands and the localized magnetic behavior.

The more widely accepted view, which is supported by band-structure calculations,^{14,15} is that the $4s$ band is well above the Fermi level and that only states in the t_{2g} subband of the $3d$ -band are occupied by the electrons. The most important effect of the Coulomb interaction is that due to intra-atomic Coulomb interactions which are described by a Hubbard model. Let us consider the specific case of V_4O_7 where detailed crystallographic evidence is available. In this compound the average valence is $V^{3.5+}$. If all sites were equivalent, then one would be dealing with a $\frac{1}{4}$ -filled band. Based on the Hubbard model, one would expect only metallic behavior and ferromagnetic interactions^{16,17} in clear contradiction to the observed *antiferromagnetic* interactions. However, all sites are not equivalent in the crystal structure. The four inequivalent sites are split into two groups³: sites (3) and (4), which are at the shear plane, and sites (1) and (2), which are close to the center of the rutile block. These two groups of sites are distinguished by their different V-V coordinations and presumably by different values of the transfer integrals and possibly by different energies for the d levels. The effect of the former complications on the Hubbard model have not been examined, but the last problem has been investigated by Rice and Brinkman.¹⁸ These authors have

shown that a metal-insulator transition is possible if the energy splitting t_0 between the atomic levels on different sites and the intra-atomic Coulomb energy U are both large enough. If in the metallic state t_0 is large and comparable to the bandwidth, then only the subband corresponding to two of the four sites will be occupied. In such circumstances there would be effectively a Hubbard model with a half-filled band and antiferromagnetic interactions would result. However, this model would require an almost complete charge differentiation between the sites (3), (4) and the sites (1), (2), contrary to experiment as shown above. Thus it appears that even a modified Hubbard model will not be consistent with both the crystallographic and magnetic experimental facts.

The crystallographic evidence shows a slight charge difference between sites (1), (3) and (2), (4) (see Fig. 1). The pattern is similar to that of the charge localization in the insulating phase. Now sites (1) and (2), and also sites (3) and (4), are not differentiated by their V-V coordination but only by the difference in V-O distances. The relaxation of the V-O distance will cause a level splitting t_0 which can be viewed as a polaron effect. If the polaron effects predominate, then we could view the metallic phase as a nondegenerate gas of small polarons. This implies that the polaron-narrowed bandwidth is $\lesssim 100$ °K. The crystal can then be viewed as a random mixture of V^{3+} and V^{4+} sites with (2) and (4) having 60% probability of occupation by the extra electron. The conductivity values of 10^3 mho cm^{-1} imply mobilities of order 10^{-1} $\text{cm}^2/\text{V sec}$, which is too high for small polarons. A further difficulty with a small-polaron model is that if it applies to the Magnéli phases, it should apply also to the single-valence oxides VO_2 and V_2O_3 . Detailed studies in the former material have determined mobilities as high as 0.5 $\text{cm}^2/\text{V sec}$,¹⁹ much larger than the values characteristic of small polarons. Further, if we assume a very substantial band narrowing due to polaron effects so that the metallic state is nondegenerate, then the thermopower α should be given by

$$\alpha = -(k_B/e) \ln[2/(n-2)]$$

for $V_n\text{O}_{2n-1}$. These values are much larger than the values $\alpha \lesssim 10$ $\mu\text{V}/^\circ\text{K}$ reported in Ref. 2. These values are typical of a poor metal. To sum up, while a small-polaron model may explain the magnetic data, it is inconsistent with the transport data. We do not presently have a plausible theoretical picture of the metallic phases. As pointed out earlier, the magnetic behavior of the mixed-valence oxides with d^0 and d^1 configurations is markedly less localized than those with d^1 and d^2 , which may indicate that Hund's-rule coupling plays an important role.

The main characteristic of the insulating phases is the charge localization into two interpenetrating lattices of different charges. In $V_4\text{O}_7$ the charge differentiation is into a V^{3+} string and a V^{4+} string. Note there is no tendency for the V^{3+} sites to be at shear planes where the local symmetry is close to corundum. The driving mechanism for this transition appears to be the V-O coupling. The form of the charge localization is such that V-O distances contract simultaneously around all V^{4+} chains and expand around all V^{3+} chains. This relaxation of the oxygen atoms will give rise to a splitting t_0 between the d levels in the two sites. If t_0 becomes comparable to the bandwidth, then as shown by Rice and Brinkman,¹⁸ a Mott-Hubbard insulator can result. The insulating state may then be viewed as a charge density wave state. It appears in all cases that some V sites, particularly V^{4+} , are always paired in the insulating phase. The additional energy gained by this pairing will help to stabilize the insulating phase. The insulating phase is initially a mixture of paired and localized V sites and at the antiferromagnetic transition the localized sites become ordered.

In these compounds, because of their low symmetry, there is no change in symmetry between the metal and insulating phases. Therefore, the metal-insulator transition may be first order or continuous. In the case of $V_4\text{O}_7$ the transition is only weakly first order, and it is possible that by applying pressure it could become continuous. It is clear from the Knight-shift data that the pairing of the V^{4+} appears to vary as an order parameter as the transition is approached. A proper model of the transition, however, must await more understanding of the metallic phase. In particular, it is not clear whether the localized magnetic behavior implies a large spin entropy and a large entropy of mixing from the V^{4+} and V^{3+} sites.

V. CONCLUSIONS

Our measurements of the local spin susceptibilities in metallic $V_7\text{O}_{13}$ and $V_4\text{O}_7$ show that, although the local susceptibility behavior is essentially local-moment-like, the sites are not differentiated into $S = \frac{1}{2}$ and $S = 1$ spins. Charge transfer between the sites occurs sufficiently rapidly to narrow the observed nuclear resonances into well-defined lines. The associated tendency for equalized charges on the inequivalent sites in the metallic state and more differentiated 3+ and 4+ behavior in the insulating state offers a means for driving the metal-insulator transitions. The intra-atomic Coulomb interactions alone cannot account for the metal-insulator transition. However, if a sufficiently large energy splitting develops between the d levels in two sublattices, then a transition to the insulating phase is possible. This resultant charge

localization causes a change in the vanadium oxygen distances which in turn can act in a self-consistent manner to produce the energy splitting between the d levels. The vanadium-oxygen interatomic Coulomb interaction would appear to be an important new driving force for the transition to the insulating state.

Also observed on transition to the I state in all the mixed-valence vanadium oxides is a singlet spin pair bonding of some sites. In no case, however, does the antiferromagnetic ordering transition temperature correspond to the metal-insulator transition, nor does the antiferromagnetism destroy the singlet pair bonds of an insulating state. The singlet pairing interaction thus exceeds the antiferromagnetic interactions and provides an additional driving force for the metal-insulator transition. No model which relies on simply splitting bands by virtue of structural distortions can adequately account for these phenomena and the metal-insulator transitions.

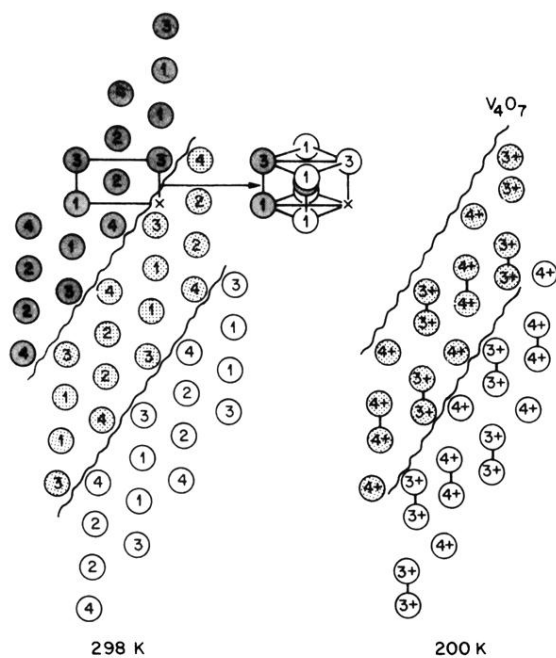
The magnetic susceptibilities of the metallic

phases of all the Magnéli phases are higher and more nearly local-moment-like than in either VO_2 or V_2O_3 . The Weiss θ 's are all of order 50°K . This behavior is difficult to understand on the basis of uncorrelated energy bands, since the required bandwidths would also have to be of the order 50°K or 0.01 eV . Neither the transfer integrals suggested by the vanadium to vanadium distances nor the observed thermoelectric powers are consistent with such narrow bands. At present, we do not have a plausible theoretical model which accounts for these remarkable properties of the metallic phases of the mixed valence oxides.

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AVERAGE METAL OXYGEN DISTANCE Å
EACH OCTAHEDRON

ATOM	298 K	200 K	PREDICTED
1	1.967 (2)	1.948 (2)	1.94 V ⁴⁺
2	1.980 (2)	1.992 (2)	2.01 V ³⁺
3	1.969 (2)	1.961 (2)	1.94 V ⁴⁺
4	1.984 (2)	2.009 (2)	2.01 V ³⁺

FIG. 1. Structure diagram from Ref. 20 for V_4O_7 in metallic phase (298°K) and insulating phase (200°K). The diagram shows the pattern of charge localization (+3, +4) and pairing of vanadium ions (heavy lines) in the insulating phase and the undistorted structure of the metallic phase. The numbers in the center figure designate the crystallographically inequivalent sites.