

## Microscopic magnetic properties of vanadium oxides. II. $V_3O_5$ , $V_5O_9$ , $V_6O_{11}$ , and $V_6O_{13}$

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The local distributions of magnetization in  $V_3O_5$ ,  $V_5O_9$ ,  $V_6O_{11}$ , and  $V_6O_{13}$  have been determined in their metallic, insulating, and antiferromagnetic insulating phases by means of  $^{51}\text{V}$  nuclear magnetic resonance. Magnetic inequivalence of atomic sites is found in each phase. At every metal-insulator transition, radical changes in local magnetic properties occur. Increased charge differentiation and localized-moment or spin-paired behavior are found in the insulating phases. In the metallic phases, partial charge differentiation and strongly correlated narrow-band behavior are observed.

### INTRODUCTION

The existence of compounds of mixed valence with transitions from metallic to insulating behavior adds an interesting new dimension to the problem of metal-insulator transitions. In compounds with only one valence state for the metal ions, the charge-transfer processes needed for metallic conductivity are costly in Coulomb energy. But in compounds with several metal-ion valence states, transfer of charge between sites of different valence can be of lower energy. In spite of this process, a number of mixed-valence transition-metal oxides have been found to undergo transitions to an insulating state. In order to examine such processes and transitions, it is desirable to use a probe which might resolve the spin and moment distributions of the inequivalent sites. We report here nuclear-resonance studies of a series of such mixed-valence vanadium oxides, most of which have metal-insulator transitions.

In a previous paper (I),<sup>1</sup> we studied the mixed 3+ and 4+ valence compounds  $V_4O_7$  and  $V_7O_{13}$  by means of magnetic susceptibility and nuclear magnetic resonance.  $V_4O_7$  showed a transition to an insulating state, and both compounds showed remarkably local-moment-like magnetic properties in the metallic state. Here we extend the study to three of the same series of Magnéli-phase compounds,  $V_3O_5$ ,  $V_5O_9$ , and  $V_6O_{11}$ , as well as to the  $V^{4+}$ - $V^{5+}$  compound  $V_6O_{13}$ .  $V_7O_{13}$  was metallic at all temperatures.  $V_3O_5$  is thought to remain semiconducting in the accessible range of temperature. All of the other compounds undergo metal-insulator transitions and at lower temperatures order antiferromagnetically.<sup>2-4</sup> In each compound, we have observed nuclear magnetic resonance of  $^{51}\text{V}$  in the metallic, insulating, and antiferromagnetic states and have used the spectra to determine the site distribution of magnetization. A first-order change

in distribution of magnetic moment accompanying the metal-insulator transition is again observed in all of the newly studied compounds with such transitions. In every case, singlet pairing of moments on some sites develops in the insulating state and is found to persist even in the antiferromagnetic state. In the metallic state, nearly localized magnetism is seen, as in I, and two types of inequivalent sites, only partially differentiated into 3+ and 4+ character, are observed. Insulating-state spin pairing and metallic-state localized magnetic behavior are also seen in the chainlike  $V_6O_{13}$  structure, which has  $V^{4+}$ - $V^{5+}$  composition. The problems encountered in  $V_4O_7$  (Ref. 1) are now found to extend to other Magnéli-phase compounds and to  $V_6O_{13}$ . They involve the inadequacy of the simple Hubbard model in explaining the transition and the unusually local-moment-like behavior of the metallic state.

### EXPERIMENTAL

Samples of  $V_3O_5$ ,  $V_4O_7$ ,  $V_5O_9$ ,  $V_6O_{11}$ ,  $V_7O_{13}$ , and  $V_6O_{13}$  were prepared by reaction of weighed mixtures of  $V_2O_3$  and  $V_2O_5$  as described in Ref. 2. The  $V_6O_{13}$  susceptibility was measured by the Faraday method in an inhomogeneous magnetic field with a microbalance.<sup>5</sup> The temperature dependence of the  $V_6O_{13}$  susceptibility is shown in Fig. 1. Susceptibilities of the other samples were reported previously.<sup>3</sup>

Nuclear-resonance measurements were made with both steady-state and pulsed techniques, the steady-state measurements being made between 4 and 16 MHz with a Varian wide-line spectrometer, a blowing helium-gas temperature controller, and a signal averager for signal accumulation- and absorption-derivative integration. The integrated absorption derivatives at room temperature (metallic state except for  $V_3O_5$ ) and low temperature (insulating, not magnetically ordered state) are shown

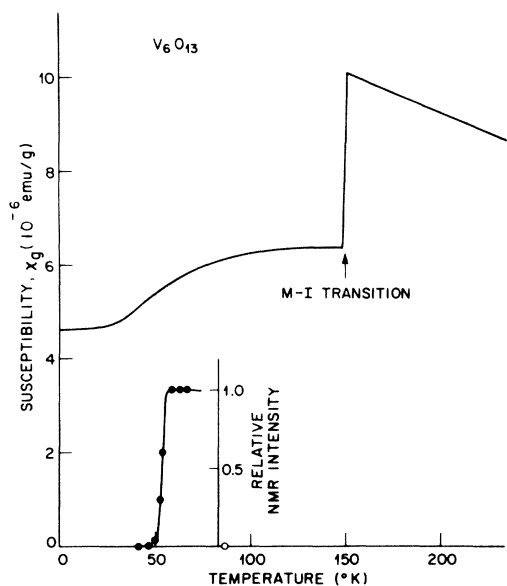


FIG. 1. Magnetic susceptibility vs temperature and relative NMR intensity vs temperature for  $V_6O_{13}$ . The decrease in NMR intensity between 50 and 60 °K is caused by the onset of magnetic long-range order. The implied Néel temperature is  $T_N = 55$  °K.

in Figs. 2 and 3. Resonance-frequency shifts were measured with respect to a  $NaVO_3$  reference solution. The temperature dependence of the several

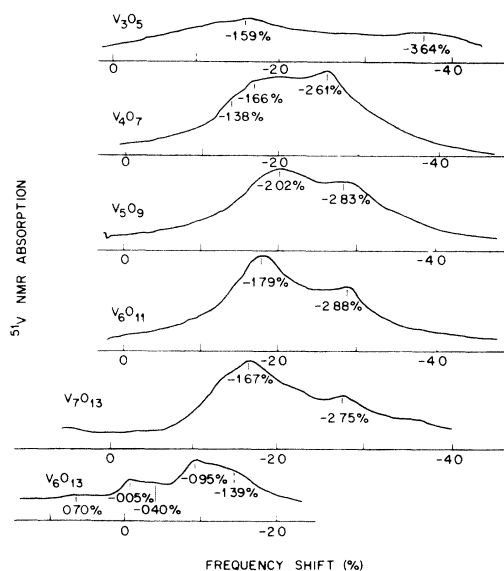


FIG. 2.  $^{51}V$  NMR absorption vs frequency shift for  $V_3O_5$ ,  $V_4O_7$ ,  $V_5O_9$ ,  $V_6O_{11}$ ,  $V_7O_{13}$ , and  $V_6O_{13}$  at 296 °K.  $V_3O_5$  is insulating while all of the other compounds are metallic at this temperature. The curves are integrals of nuclear absorption derivatives measured with steady-state techniques at a frequency of 16 MHz in an aluminum-free probe. Note relative intensity growth of less-shifted peak on passing from  $V_4O_7$  to  $V_7O_{13}$ .

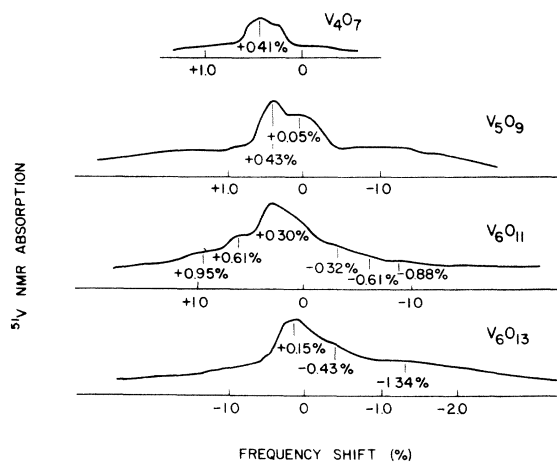


FIG. 3.  $^{51}V$  NMR absorption vs frequency shift for  $V_4O_7$ ,  $V_5O_9$ ,  $V_6O_{11}$ , and  $V_6O_{13}$  at 140 °K. All compounds are in the insulating phase at this temperature. Operating frequency is 16 MHz.

identifiable components of the  $V_6O_{13}$  spectrum are shown in Fig. 4. The pulsed measurements were made between 30 and 73 MHz using coherent detection, a transmitter power of up to 6 kW, and a 60-kOe superconducting solenoid. Frequency shifts measured by the pulsed technique in the metallic phases are shown in Table I. Spin-echo signals observed at 55 MHz in the antiferromagnetic state of the six compounds are shown in Fig. 5. The spin-echo amplitude was plotted as the field was swept. The sharp peak at 13 kOe is a proton echo from the probe and the small peak near 40 kOe is not identified. Spin-echo measurements were also made with zero applied field in the antiferromagnetic state, using the internal hyperfine field of the antiferromagnetic sublattice magnetization to provide the dc magnetic field for resonance. Signals were seen in  $V_3O_5$ ,  $V_5O_9$ , and  $V_6O_{13}$  in zero

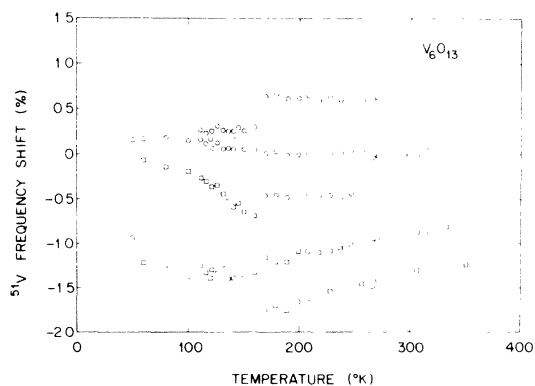


FIG. 4.  $^{51}V$  NMR frequency shifts vs temperature for  $V_6O_{13}$ . Circles are associated with (5+)-like sites ( $d^0$ ) and squares with (4+)-like sites ( $d^1$ ).

TABLE I. Metallic-state frequency shifts from spin-echo measurements.

Sample	$T$ ( $^{\circ}\text{K}$ )	$^{51}\text{V}$ frequency shift (%)
$\text{V}_4\text{O}_7$	250	-2.2
$\text{V}_5\text{O}_9$	250	-2.4
$\text{V}_6\text{O}_{11}$	250	-2.2
$\text{V}_7\text{O}_{13}$	77	-4.5, -5.5, -7.7, -10.7
$\text{V}_6\text{O}_{13}$	250	0, $\sim -1$

field with the resultant spectrum of echo amplitude vs frequency shown in Fig. 6. The 190-MHz echoes were seen with an incoherent detection system.

The detailed behavior found in the metallic, insulating, and antiferromagnetic states of the compounds is presented in the following sections.

#### METALLIC STATE

In all cases, local-moment-like temperature-dependent susceptibilities occur in the metallic states of these compounds.<sup>3</sup> Nuclear relaxation is quite rapid ( $T_1 \lesssim 50 \mu\text{sec}$ ), making observation of metallic-state nuclear spin echoes quite difficult

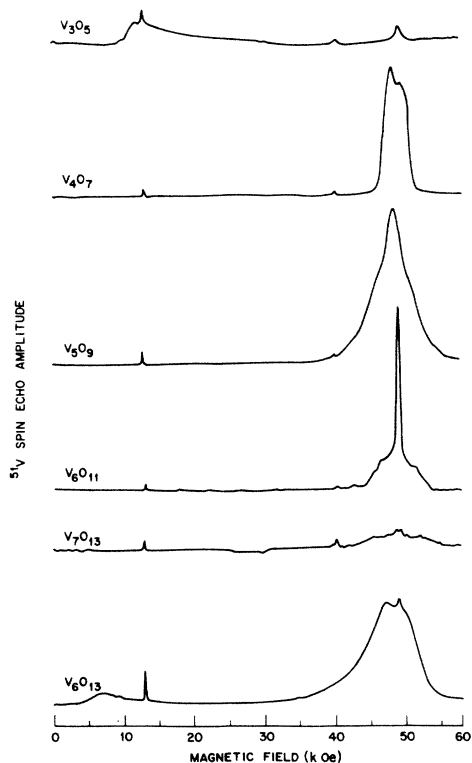


FIG. 5.  $^{51}\text{V}$  spin-echo amplitude vs magnetic field at 55.0 MHz and 4.2 K for  $\text{V}_3\text{O}_5$ ,  $\text{V}_4\text{O}_7$ ,  $\text{V}_5\text{O}_9$ ,  $\text{V}_6\text{O}_{11}$ ,  $\text{V}_7\text{O}_{13}$ , and  $\text{V}_6\text{O}_{13}$  in the antiferromagnetic state. Sharp responses at 12.9 kOe are from protons in probe.

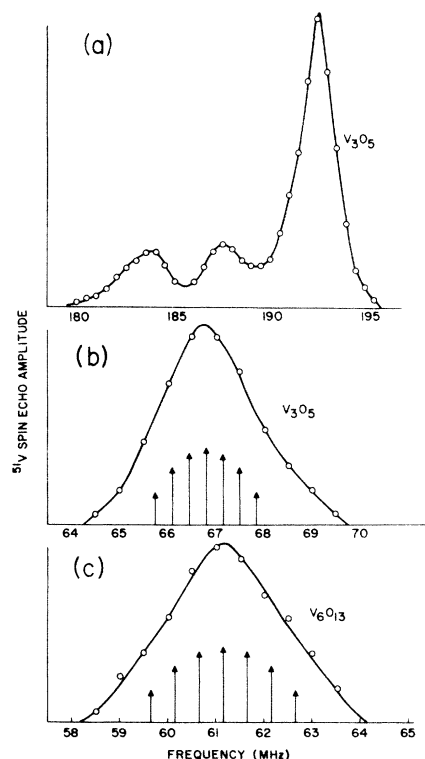


FIG. 6. Zero-field antiferromagnetic-state NMR spin-echo spectra of  $^{51}\text{V}$  in  $\text{V}_3\text{O}_5$  and  $\text{V}_6\text{O}_{13}$  at 4.2 K. Positions of arrows indicate first-order quadrupole satellite frequencies. Peak near 12 kOe in  $\text{V}_3\text{O}_5$  is associated with shifted 67-MHz zero-field resonance shown in Fig. 6 and  $\text{V}_6\text{O}_{13}$  peak near 6 kOe with 61-MHz zero-field resonance.

except for the echoes from the nonmagnetic site of  $\text{V}_6\text{O}_{13}$ . For all the Magnéli-phase compounds, two predominant negatively shifted steady-state nuclear-resonance components were found. The observation of two lines shows immediately that all sites are not equivalent magnetically. In I we assigned the more-shifted lines to sites with more  $d$  electrons [more (3+)-like sites] and the less-shifted line to more (4+)-like sites.<sup>6</sup> The steady increase in intensity of the less-shifted line relative to the more-shifted component, on moving from  $\text{V}_4\text{O}_7$  to  $\text{V}_7\text{O}_{13}$  accompanies a stoichiometric increase of 4+ sites on passing toward  $\text{V}_7\text{O}_{13}$  and confirms this assignment. Susceptibility values for the two types of sites, derived from the NMR shifts by using ionic hyperfine coupling constants, are shown in Table II. The coupling constants used are  $-120$  and  $-85 \text{ kOe}/\mu_B$  for  $3d$  spin moments of 3+ and 4+ sites, respectively.<sup>1</sup> Temperature-independent orbital-frequency-shift components of +1.2 and +0.3% are assumed for 3+ and 4+ sites. The total susceptibility derived in this manner is in rough agreement with the observed susceptibility. The susceptibilities of the inequivalent sites do not

TABLE II. Vanadium NMR frequency shifts and local magnetic susceptibilities for (3+)-like and (4+)-like sites in  $V_nO_{2n-1}$  at 296 °K.

	$K_{\text{spin}}^{3+}$ <sup>a</sup>	$K_{\text{spin}}^{4+}$ <sup>b</sup>	$(\chi_{\text{spin}}^{3+})_{\text{NMR}}$ <sup>c</sup> ( $10^{-4}$ emu/mole)	$(\chi_{\text{spin}}^{4+})_{\text{NMR}}$ <sup>d</sup> ( $10^{-4}$ emu/mole)	$(\chi_{\text{spin}})_{\text{NMR}}$ <sup>e</sup> ( $10^{-4}$ emu/mole)	$\chi_{\text{obs}}$ ( $10^{-4}$ emu/mole)
$V_3O_5$	-0.0484	-0.0189	15.0	4.1	19.1	17.1
$V_4O_7$	-0.0381	-0.0182	8.9	6.0	14.9	19.8
$V_5O_9$	-0.0403	-0.0232	7.5	9.2	16.7	20.8
$V_6O_{11}$	-0.0408	-0.0209	6.3	9.2	15.5	23.3
$V_7O_{13}$	-0.0395	-0.0197	5.3	9.3	14.6	18.6
$V_8O_{13}$	...	-0.0147	...	6.4	6.4	5.3

$$^a K_{\text{spin}}^{3+} = K_{\text{obs}}^{3+} - 0.012.$$

$$^b K_{\text{spin}}^{4+} = K_{\text{obs}}^{4+} - 0.003.$$

$$^c (\chi_{\text{spin}}^{3+})_{\text{NMR}} = -(2A\mu_B K_{\text{spin}}^{3+} / 0.120 \times 10^6 n) \text{ emu/mole of } V_nO_{2n-1}.$$

$$^d (\chi_{\text{spin}}^{4+})_{\text{NMR}} = -[(n-2)A\mu_B K_{\text{spin}}^{4+} / 0.085 \times 10^6 n] \text{ emu/mole of } V_nO_{2n-1}.$$

$$^e (\chi_{\text{spin}})_{\text{NMR}} = (\chi_{\text{spin}}^{3+})_{\text{NMR}} + (\chi_{\text{spin}}^{4+})_{\text{NMR}} \text{ emu/mole of } V_nO_{2n-1}.$$

differ by as large a factor as the  $S(S+1)$  expected for  $S = \frac{1}{2}$  and  $S=1$  localized paramagnetic moments, showing that 3+/4+ differentiation is incomplete in the metallic state or that the Weiss  $\theta$  is larger for the more magnetic sites. As stressed I, the resolution of signals from sites with nonintegral charge shows that there is a rapid charge exchange between the inequivalent sites, but with the time-average charges being different on the two sites. The rapid nuclear relaxation which made spin-echo observability difficult may result from either relaxation by conduction electrons or relaxation by local moments. It is unfortunate that  $T_1$  could not be measured since a study of its temperature dependence and magnitude could help to differentiate local-moment and itinerant magnetization behavior.

In metallic  $V_6O_{13}$ , three lines tentatively identified as a first-order quadrupole-split response from a nonmagnetic site with close to zero  $d$  electrons were found in the steady-state measurements. The deduced quadrupole interaction is  $\nu_Q = e^2qQ/14h = 0.18$  MHz. The splitting of the three lines is frequency independent from 6 to 16 MHz. Two unresolved negatively shifted peaks, which we assign to two more nearly (4+)-like sites, are also seen in the steady-state spectrum. Crystallographic studies<sup>7</sup> show three inequivalent sites in metallic  $V_6O_{13}$  which can be identified with the three NMR lines. In pulsed studies, a strong spin echo near zero frequency shift and a broad, weak, negatively shifted satellite were seen, again in agreement with the steady-state results.

#### INSULATING STATE

The metal-insulator transitions in these compounds are first order, with a definitely lower susceptibility in the insulating state. The only nuclear-resonance lines and echoes that could be detected in the insulating states of the Magnéli compounds were slightly positive-shifted lines apparently derived from nuclei on 4+ sites with singlet-

paired 3d spins. In  $V_6O_{13}$ , though, all three resonance lines could be detected including signals from both magnetic and nonmagnetic sites. In  $V_3O_5$ , only very wide and weak negatively shifted lines could be seen, showing that no sites are paired in this compound and all are magnetic in origin. Quadrupole modulation of the spin-echo amplitude could be resolved in a number of cases, with  $\nu_Q = 0.62$  MHz in  $V_4O_7$ , 0.79 MHz in  $V_5O_9$ , and 0.79 MHz in  $V_6O_{11}$ . For comparison, in  $V_2O_3$ ,  $\nu_Q = 0.51$  MHz.

The  $V_6O_{11}$  steady-state spectrum showed a series of weak satellites on either side of the peak center with spacing  $\sim 0.3\%$ . The expected fractional spacing between first-order quadrupole satellites would be  $\nu_Q/2\nu_L = 0.79/2(16) = 2.5\%$  for the operating conditions, so the observed splittings are too small to be first-order quadrupole satellites. The increased number of detectable satellites and increased overall breadth of the spectrum on moving from  $V_4O_7$  to  $V_5O_9$  to  $V_6O_{11}$  probably results from the increased number of inequivalent sites in  $V_5O_9$  and  $V_6O_{11}$ . Anisotropic orbital shifts and negative components of frequency shift on sites with incompletely paired spins could produce  $V^{4+}$  spectra with the general shape observed and seem the most probable source of the observed structures.

In insulating  $V_6O_{13}$ , a definite absorption at  $-1.34\%$  frequency shift is observed. This must be assigned to paramagnetic 4+ sites with paramagnetic spins of  $\frac{1}{2}$ . Two unresolved lines about  $K = +0.15\%$  and a line with a temperature-dependent shift of  $-0.43\%$  are also seen. The former may derive from 4+ sites with singlet-paired spins and the latter from a site becoming progressively more 5+, i.e., losing its 3d electron density on cooling. An alternate assignment with the first site (5+)-like and the second site pairing increasingly on cooling would also be possible, however, and we are unable to distinguish definitely between the two possibilities at this time.

The most important feature of the insulating-state nuclear resonances is the change in the resonance from negatively shifted in the metallic regimes to slightly positively shifted in the insulating state for  $V_4O_7$ ,  $V_5O_9$ , and  $V_6O_{11}$ . This demonstrates the development of spin-paired sites with reduced local susceptibility. The simultaneous existence of strongly shifted magnetic sites whose resonance is not visible is required in order to produce the observed susceptibilities of the insulating state. The resonance of the magnetic site in insulating  $V_6O_{13}$  is barely visible, presumably because it is a  $d^1 S = \frac{1}{2}$  site and consequently has a narrower resonance than the  $d^2 S = 1$  magnetic sites in the Magnéli phases.

#### ANTIFERROMAGNETIC STATE

In  $V_3O_5$ , where no spin-paired sites were found in the paramagnetic states, two zero-applied-field nuclear-resonance spin-echo signals were found in the antiferromagnetic state. These can be associated with  $V^{3+}$  sites and  $V^{4+}$  sites. The  $V^{3+}$  response consisted of a strong main line ( $m$ ) and two satellites ( $S_1$  and  $S_2$ ), with the spin-echo decay of all lines strongly modulated with frequency  $\delta\nu_{\text{mod}}$  by quadrupole interactions. The observed spectra of echo envelope vs frequency are shown in Fig. 6(a). Taking a frequency-hyperfine-field ratio of 1.1193 kHz/Oe for  $^{51}\text{V}$  gives for the hyperfine fields for the main line and satellites  $H_N^m = 172.2 \pm 0.2$  kOe ( $\delta\nu_{\text{mod}} = 0.17$  MHz),  $H_N^{S_1} = 167.5$  kOe ( $\delta\nu_{\text{mod}} = 0.22$  MHz), and  $H_N^{S_2} = 164.2$  kOe ( $\delta\nu_{\text{mod}} = 0.23$  MHz). The  $V^{4+}$  spin-echo spectrum shown in Fig. 6(b) yielded  $H_N = 59.7 \pm 0.3$  kOe ( $\delta\nu_{\text{mod}} = 0.36$  MHz). A recent inelastic spin-flip neutron scattering measurement of the average hyperfine field in  $V_3O_5$  gave a value of  $146 \pm 6$  kOe.<sup>6</sup> The neutron result is less accurate than the present results and does not distinguish the inequivalent sites. The neutron value is intermediate between the  $V^{3+}$  and  $V^{4+}$  hyperfine fields, but somewhat larger than the average of 135 kOe obtained from the spin-echo measurements. When the  $^{51}\text{V}$  spin-echo amplitude in  $V_3O_5$  at 55 MHz was monitored while the magnetic field was swept, an echo edge near 12 kOe was seen, associated with  $V^{4+}$  sites with hyperfine field antiparallel to applied field. A weak echo near  $\omega/\gamma$  is associated with impurity  $V^{5+}$  atoms. There is no evidence for any singlet-paired sites in the antiferromagnetic state.

In antiferromagnetic  $V_4O_7$ , as reported earlier, echoes from two magnetic  $V^{4+}$  sites were found with hyperfine fields 70.1 and 78.4 kOe. One nonmagnetic paired site with hyperfine field 1.74 kOe was also reported. Magnetic  $V^{3+}$  sites were not detected but may exist.

A very weak spin echo from antiferromagnetic  $V_5O_9$  corresponding to a magnetic site with  $H_N = 138$  kOe was observed. A strong echo from a

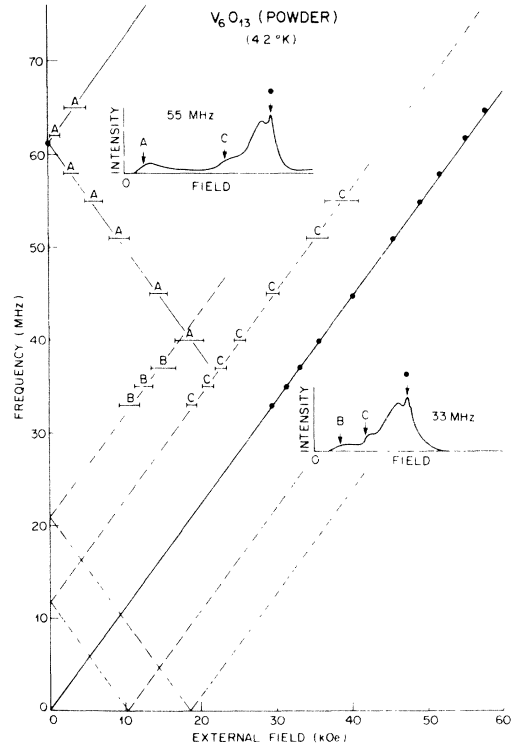


FIG. 7. Position of  $^{51}\text{V}$  spin-echo-amplitude powder pattern peaks as a function of external field for various operating frequencies.

nonmagnetic paired site was seen in an applied field with 4.2 °K frequency shift ( $+0.34 \pm 0.10$ )%, a hyperfine field  $H_N = 4.2 \pm 0.4$  kOe, and a quadrupole interaction  $\nu_Q = 0.79 \pm 0.10$  MHz. The powder pattern for the site was peaked at the center and distributed symmetrically, in contrast to  $V_4O_7$ , where a double-peaked spectrum was observed. Such behavior is to be expected if the angle between the hyperfine field and the electric field gradient on the observed nonmagnetic site is zero for  $V_5O_9$  and  $\pi/2$  for  $V_4O_7$ . Only the nonmagnetic-site nuclear spin echoes were observed in antiferromagnetic  $V_6O_{11}$ . The spectrum was similar to the  $V_5O_9$  case with 4.2 °K frequency shift ( $+0.34 \pm 0.10$ )%,  $H_N = 4.2 \pm 0.4$  kOe, and  $\nu_Q = 0.79 \pm 0.10$  MHz. The antiferromagnetic state of  $V_7O_{13}$  is metallic. No definite nuclear resonances could be detected, showing that there is no paired site in the  $V_7O_{13}$  structure. Both magnetic- and nonmagnetic-site spin echoes were seen at 4.2 °K in  $V_6O_{13}$ . The completely unpaired  $V^{4+}$  site which is the main source of antiferromagnetism gave a hyperfine field  $H_N = 54.7 \pm 0.3$  kOe, with  $\delta\nu_{\text{mod}} = 0.50$  MHz, observed in zero applied field [Fig. 6(c)]. Two somewhat less magnetic sites with  $H_N = 20$  kOe and  $H_N = 10$  kOe were also seen (Fig. 7). In addition to these lines from magnetic sites, a line from an

almost nonmagnetic site was seen in an applied field. Its width of 6 kOe suggests a hyperfine field  $H_N \approx 3$  kOe. However, unlike the Magnéli-phase nonmagnetic responses, this line was shifted to lower fields by 1.6 kOe independent of operating frequency. This suggests a possible field-independent partial alignment of spins and moments, although no evidence for such behavior was seen in the magnetic susceptibility.

The essential nuclear-resonance result for the antiferromagnetic state of these compounds is that three distinct classes of sites can be differentiated: (i)  $V^{3+}$  sites with hyperfine fields 150 to 200 kOe, (ii)  $V^{4+}$  sites with hyperfine fields near 50 kOe, and (iii) nonmagnetic paired (or  $V^{5+}$  for  $V_6O_{13}$ ) sites with transferred hyperfine fields of a few kOe. Only in  $V_7O_{13}$  and  $V_3O_5$  are paired sites not found. In  $V_7O_{13}$ , this is because no transition to an insulating state occurs. In  $V_3O_5$  a structural explanation probably applies because  $V^{4+}$  sites, occupying a plane intermediate between  $V^{3+}$ -like shear planes, are not in close enough proximity to promote pairing.

#### CONCLUSIONS

The present study of a series of related compounds illuminates some of the systematic features of metal-insulator transitions in vanadium oxides. The metallic states of all the compounds studied here show strongly temperature-dependent magnetic susceptibilities. The nuclear-resonance measurement of the local site susceptibilities reveals inequivalent sites but show that the susceptibility difference between sites is smaller than expected for

$S = \frac{1}{2}$  and  $S = 1$  local moments appropriate to  $d^{1,0}$  and  $d^{2,0}$  ionic configurations. The appropriate model for the metallic state is then not a purely local-moment picture, but one with very narrow, strongly correlated  $d$  bands. We do not have an appropriate, detailed model of such a state though. A simple Hubbard-type model, in which correlations are the prime driving force for a metal-insulator transition, is insufficient to explain the magnetic behavior and transitions, since it would produce ferromagnetic correlations or else require complete  $3+/4+$  charge differentiation.<sup>1</sup> Also, as in  $V_4O_7$ , polaron effects do not seem capable of explaining the behavior of the metallic state<sup>1</sup> because they would require such a narrow band that they would reduce mobilities far below the observed values.

The insulating states are characterized by increased charge localization, together with singlet pairing of spins on some site (except for  $V_3O_5$ ). Both of these effects serve to stabilize the insulating state, since the charge localization and associated changes in the vanadium-oxygen Coulomb interaction will split the  $d$  subbands associated with the sites, leading to Mott-Hubbard insulating behavior,<sup>9</sup> while the pairing will produce a further lowering of the insulating-state energy. The pairing-energy lowering is sufficiently large that even the transitions to antiferromagnetic states do not destroy the singlet behavior.

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