PHYSICAL REVIEW B VOLUME 20, NUMBER 7 1 OCTOBER 1979

Susceptibilities of the vanadium Magnéli phases V_nO_{2n-1} at low temperature

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(Received 7 May 1979)

The magnetic susceptibilities of the insulating Magnéli phases V_3O_5, V_4O_7, V_6O_{11}, and V_8O_{15} have been measured at low temperatures. Due to a short-range-order effect V_3O_5 exhibits a broad maximum at 125 K, which is substantially higher than the Néel temperature, 76 K, of this compound. For V_4O_7 and V_6O_{11} the difference between the Néel temperature and the temperature of the maximum in the susceptibility is small. This excludes the possibility that a linear-chain model discussed by Khattak *et al.* can explain the specific heat of these two compounds. The temperature derivative of the susceptibility for these two compounds has a maximum at the Néel temperature which corresponds to Fisher's relation. The susceptibility for V_8O_{15} is nearly constant between 5.6 and 68 K, and depends on past history below 5.6 K, i.e., whether the sample is being cooled or heated. However this temperature hysteresis is sample dependent. These experimental data cannot be accounted for by an ordinary antiferromagnetic transition in the insulating state and suggest another type of transition. The possibility of the existence of a mixed charge-density and spin-density wave is discussed, since this can explain qualitatively the experimental features found for V_8O_{15}.

I. INTRODUCTION

Between V_2O_3 and VO_2 are intermediate compounds, called Magnéli phases, which can be expressed by the formula V_nO_{2n-1} $(3 \leq n \leq 9)$. They show a temperature-induced metal-insulator transition at T_t (except V_7O_{13}, which remains metallic down to 4 K), and an antiferromagnetic transition at lower temperature T_N.[1] In these Magnéli phases T_t and T_N occur at different temperatures for each value of n and especially the Néel temperature T_N changes rather smoothly with n, see Table I. The chemical formula for these Magnéli phases can be written as $V_nO_{2n-1} = V_2O_3 + (n-2)VO_2$, so that, if complete ionic character is assumed the valence of the vanadium ions is 3+ or 4+. At room temperature the crystal structure of V_3O_5 is monoclinic, while the phases with $n \geq 4$ are triclinic.[2–4] The structure consists of a distorted hexagonal close-packed array of oxygen and belongs to a shear structure based on the rutile lattice. For the insulating state the detailed crystal-structure refinements using x-ray diffraction have been done for V_4O_7,[5,6] and V_5O_9,[7] while ^{51}V nuclear-magnetic-resonance (NMR) experiments[8,9] have been performed on most of the Magnéli phases. At the metal-insulator transition, the lattice parameters of the triclinic phase suffer small discontinuities but the intensities of some of the x-ray lines change drastically. For $T < T_t$ a characteristic feature is charge localization due to pairing of vanadium ions,[6] and some of these pairs have a spin-singlet ground state. This pairing greatly affects the magnetic and thermal properties.

The specific heats of the several Magnéli phases have been measured between 0.5 and 50 K by Khattak *et al.*[10] Their results show that the magnetic entropy change up to T_N for all these phases is less than 20% of the value $R\ln(2S+1)$ which would be expected when spin pairing is absent, and so indicate a considerable singlet spin pairing. The present work is concerned with the low-dc-field magnetic susceptibility of V_nO_{2n-1} for their insulating states.

TABLE I. Magnéli phases of mixed-valence compounds with d^1 and d^2 configurations, the temperature of the metal-insulator transition T_t, and the Néel temperature T_N.

V_nO_{2n-1}	Number of cations V^{3+} $(S=1)$	 V^{4+} $(S=\frac{1}{2})$	T_t (K)	T_N (K)
V_2O_3	2	0	155	155
V_3O_5	2	1	430[a]	76[b]
V_4O_7	2	2	238	33.3
V_5O_9	2	3	135	28.8
V_6O_{11}	2	4	170	24.0
V_7O_{13}	2	5	· · ·	43.0
V_8O_{15}	2	6	68	6.1[c]
⋮				
VO_2	0	1	340	

[a] From Ref. 33.
[b] From Ref. 13.
[c] This transition might not be an ordinary antiferromagnetic one, see text.

II. EXPERIMENTAL

The susceptibilities of the four Magnéli phases were measured on subsets chosen from the crystals used for the specific-heat investigation by Khattak *et al.*[10] These are single crystals grown by the chemical transport method using $TeCl_4$ as the transport agent following a description by Nagasawa.[11] In an attempt to dampen excessive chemical fluctuations near the crystal growing surface, more than 0.1 bar argon or xenon was used in the capsules. The samples were identified by x-ray powder diffraction, and by Laue x-ray pictures. For each susceptibility measurement several small crystals were used with a total mass of 20 to 30 mg; their orientations were random.

Changes in magnetization as a function of temperature were measured at a constant applied field with a superconducting quantum interference device (rf-SQUID); the details of the experimental method have been described elsewhere.[12] Changes in the magnetization were linear proportional to the applied fields between 2 and 40 Oe, and were converted to susceptibility χ. The magnitude of the susceptibility change was calibrated by placing adjacent to the samples a small piece, about 0.5 mg, of Pb or Ta. Additionally, the change in the superconductive transition temperature gave a check on the calculated value of the applied field. Temperature was monitored by a previously calibrated germanium thermometer. The SQUID system is ideally suited for measuring changes in susceptibility, but not so well suited for acquiring the absolute magnitude and consequently the temperature-independent susceptibility, χ_0, can contain appreciable errors.

III. RESULTS AND DISCUSSION

A. V_3O_5

The susceptibility versus temperature of V_3O_5 in an applied field of 10 Oe is shown in Fig. 1. The Néel temperature was determined by Griffing[13] using specific-heat measurements and is indicated by an arrow. The susceptibility of V_3O_5 was measured only up to 160 K, but recently Ueda *et al.*[14] reported results up to 900 K. Both these investigations show that the susceptibility has a broad maximum at $T_m = 125 \pm 5$ K, which is substantially higher than the Néel temperature $T_N = 75.5$ K. The broad maximum in susceptibility could be the result of isolated exchange-coupled spin pairs of magnetic ions, but this possibility can be excluded as NMR experiments[9] do not indicate pairing of ions for this phase. It is then probable that this broad maximum and especially the large difference between T_N and T_m is the consequence of short-range-order effects among the individual moments above T_N. The large difference between T_m and T_N of 50 K is related to the small magnetic entropy change below T_N, $\Delta S(T < T_N) = 0.15$ J/(K mole-V)[13]; this amount is less than 2% of the magnetic entropy change $R \ln(2S+1)$. Two possible sources for this short-range-order effect are suggested. One is the lowering of the dimensionality of the magnetic interaction to two or one.[15] A second possibility is the effect of valence mixing of 3+ and 4+ vanadium ions; however not enough is known about the magnetic short-range order for a system with fixed valences.

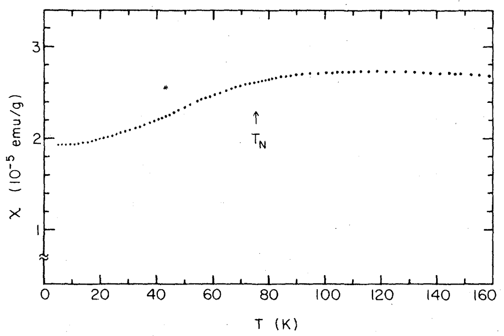

FIG. 1. Magnetic susceptibility of V_3O_5 as a function of temperature. The Néel temperature T_N (Ref. 13) is indicated.

B. V_4O_7 and V_6O_{11}

In Figs. 2 and 3 are shown the susceptibilities of V_4O_7 and V_6O_{11} in an applied field of 10 Oe. The susceptibilities above 50 K can be expressed by $\chi = C/(T - \Theta) + \chi_0$; the first term on the right-hand side is the Curie-Weiss law while χ_0 represents the temperature-independent part which contains a diamagnetic as well as a Van Vleck paramagnetic contribution. The effective number of Bohr magnetons P_{eff} per vanadium ion was deduced from the Curie constant C, assuming 2 for the Landé g factor. The

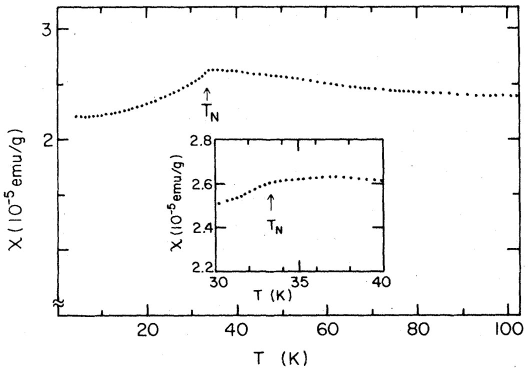

FIG. 2. Magnetic susceptibility of V_4O_7 as a function of temperature. The inset shows the susceptibility near the Néel temperature.

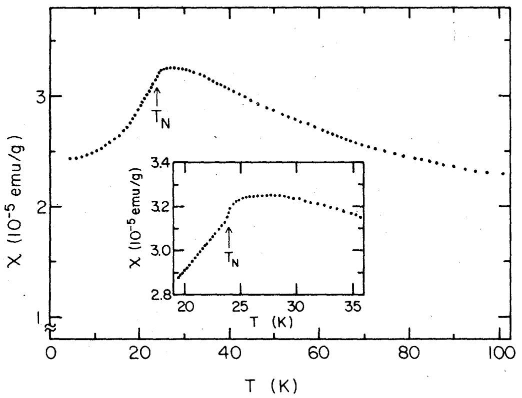

FIG. 3. Magnetic susceptibility of V_6O_{11} vs temperature. In the inset the behavior near the Néel temperature is shown.

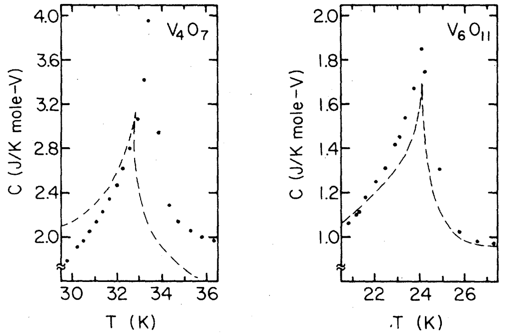

FIG. 4. Experimental comparison of the magnetic specific heat with the susceptibility gradient $\partial(\chi T)/\partial T$. The dots indicate the data of the specific heat for a mole of vanadium ion and the broken curves show the $\partial(\chi T)/\partial T$ calculated from the susceptibility in arbitrary units.

results are for V_4O_7: $P_{\text{eff}}=0.5\pm0.2$, $\Theta=-20\pm10$ K and for V_6O_{11}: $P_{\text{eff}}=0.9\pm0.3$, $\Theta=-30\pm10$ K. The errors are appreciable as it was not possible to deduce an accurate value for χ_0. We can only conclude that: (i) the two Weiss constants Θ are negative, (ii) both P_{eff} per vanadium ion are small when compared to the calculated effective numbers of Bohr magnetions of these two mixed valence compounds. In the absence of spin pairing, these numbers are 2.35 and 2.16 for V_4O_7 and V_6O_{11}, respectively. This shows the reduction of the moments in these insulating phases by pairing into singlets.

The x-ray diffraction studies by Marezio *et al.*[6] on insulating V_4O_7 show a structure containing strings of V^{3+} and V^{4+} ions running parallel to the pseudorutile *c* axis. The V^{3+} sites and half of the V^{4+} sites are paired and have short vanadium-vanadium distances. The V^{4+} pair has a singlet spin, but the magnetic state of the *d* electrons involved in the V^{3+} pairing is unclear.[6,8,16] Even if $S=0$ is assumed for the V^{3+} pairs and the V^{4+} pairs,[17] the unpaired V^{4+} ions lead to $P_{\text{eff}}=0.87$ per vanadium ion, which is still larger than the experimental value. Therefore the susceptibility result indicates that the magnetic state of V^{3+} pair cannot be higher than a singlet state.

The specific heats of these two phases above T_N contain a linear term which, without the knowledge of the susceptibility, could be interpreted as the result of independent linear chains.[10] However, the results of susceptibility show that this linear chain model is untenable. This follows from the calculation of Bonner and Fisher[18] for a linear chain model of $S=\frac{1}{2}$ and assuming a Heisenberg antiferromagnetic interaction. Their results show that the specific heat is practically linear at low temperature and has a broad maximum at a higher temperature, which equals $0.96|J|/k_B$. Here J is the exchange constant and k_B is the Boltzmann constant. The susceptibility is expected to have also a broad maximum which occurs at $T_m=1.3|J|/k_B$. The susceptibility maxima in V_4O_7 and V_6O_{11} were observed at 35 and 27 K, respectively, and therefore, the linear term in the specific heat can only occur well below these temperatures, which is not in agreement with the specific heat. The difference between T_N and T_m is typically of the order of 10% of T_m in three-dimensional antiferromagnets,[15] which is the observed order for V_4O_7 and V_6O_{11}.

Using rather general arguments Fisher[19] has shown for zero magnetic field that the magnetic specific heat C_m and the susceptibility χ of an antiferromagnet are related[20-23]: $C_m=A\,\partial(\chi T)/\partial T$, where the coefficient A is a relatively slowly varying function of temperature through the region around the Néel temperature. The results of Khattak *et al.*[10] for the specific-heat data are combined with the results of the susceptibilities measured on the same samples and are shown in Fig. 4. Only the slopes of the two curves are of importance as the value of C_m (called by Khattak *et al.* C_{ex}) depends on a somewhat uncertain subtraction of the lattice contribution from the total specific heat. For V_6O_{11} the sharp peaks for both quantities C_m and $\partial(\chi T)/\partial T$ occur at the same temperature as predicted by Fisher's relation. The difference in temperature for the peaks of V_4O_7 is about one half of a degree, but this could be the result of differences in the calibration of the two thermometers used in these experiments.

C. V_8O_{15}

The susceptibility of V_8O_{15} has previously been measured by Kachi *et al.*[1]; they found a small cusp in the susceptibility at 7 K and concluded that this indicated an antiferromagnetic transition by analogy with other Magnéli phases. For the crystal set *A*, which was previously used in the specific-heat measurement by Khattak *et al.*,[10] the susceptibility above 8 K is in qualitative agreement with the data of Kachi *et al.*, but below this temperature the new results are dif-

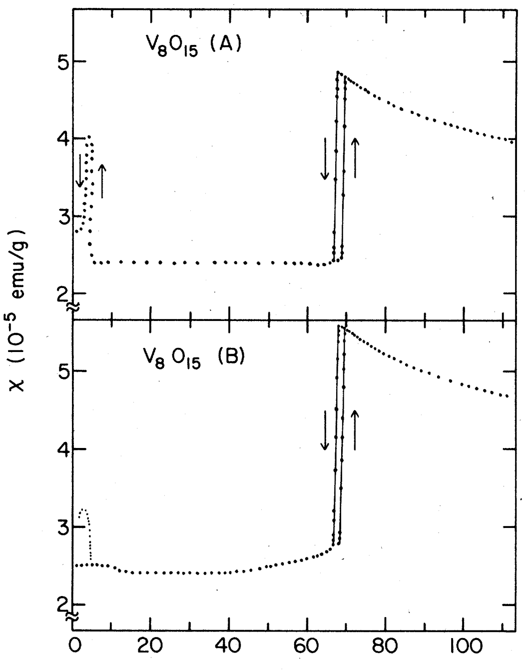

FIG. 5. Magnetic susceptibilities of V_8O_{15} vs temperature between 1 and 120 K. The arrows indicate heating or cooling. The upper- and lower-halves of the figure are results for different sample sets of *A* and *B*.

ferent from the one obtained by them. The data obtained are highly anomalous below 5.6 K as will be discussed below. To check on this different behavior a new set of crystals was grown, called *B*, for which the susceptibility and the specific heat were measured. The two crystal sets *A* and *B* were prepared by the same chemical transport method, using $TeCl_4$ as the transport agent.

The susceptibilities in an applied field of 10 Oe and the specific heats of *A* and *B* as a function of temperature are shown in Figs. 5 and 6. The experimental features are as follows: (i) Above T_t, in the metallic state, χ has a stronger temperature dependence than the single valence compounds V_2O_3 and VO_2.[1,24] (ii) The susceptibility is nearly constant between 5.6 and 68 K with $\chi = 2.4 \times 10^{-5}$ emu/g, which is larger than the Van Vleck paramagnetism found for VO_2,[1,24] or Ti_4O_7.[25,26] (iii) At low temperature the susceptibility and the specific heat are strongly sample dependent. The crystal set *A* showed nearly constant susceptibility down to 5.6 K, but below this temperature anomalous susceptibilities were observed. Two subsets of the crystals of set *B* showed a nearly constant susceptibility down to 1.2 K, but one subset also behaved anomalously, although the magnitude of the anomaly was decreased. Set *A* has a pronounced peak in the specific heat at 6.1 K, while *B* exhibits a smooth maximum at this temperature. (iv) After subtracting the lattice contribution, the entropy change up to 9 K due to the specific-heat anomaly is of the order of 0.03 J/(K mole-V). It should be noted that this entropy change is much smaller than $R\ \ln(2S+1) = 6.6$ J/(K mole-V). (v) Below 1 K, both sets *A* and *B* show a nuclear contribution to the specific heat, which is of the order of $(0.2 \text{ to } 0.4)/T^2$ mJ/(K mole-V). The rather large uncertainty is a consequence of the small heat capacity and poor thermal diffusivity. (vi) In addition the susceptibility jump and the latent heat at T_t are 2.7×10^{-5} emu/g and 91 J/mole-V, respectively. We could detect this latent heat on cooling only.

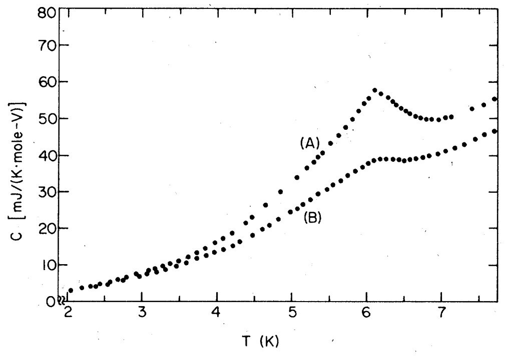

FIG. 6. Specific heats of V_8O_{15} for a mole of vanadium as a function of temperature. Data for two different sample sets *A* and *B* are shown.

The low-temperature irreversible susceptibilities of set *A* are shown in Fig. 7, and for comparison the specific heat of this set is also indicated. Below 5.6 K the susceptibility has a temperature hysteresis, i.e., dependent on cooling or heating of the sample. The arrows in Fig. 7 indicate the direction of the temperature change. To obtain more information several parameters were varied. First, the heating and cooling rate were changed. Second, time dependence was checked by keeping the sample at 4.2 K for one hour on either of the heating and the cooling branches shown in Fig. 7. Third, the magnetic field was changed between 2 and 40 Oe. No dependence was found on heating or cooling rate, the time or magnetic field. The specific heat of set *A* was independent of magnetic field up to 200 Oe and did not change if it was measured with decreasing temperature. (This latter may need some clarification. Normally in the heat-pulse method, a heat pulse will increase the temperature of the sample. However, when the sample is being cooled, a small heat pulse will temporarily slow the cooling rate, and allow the specific heat to be determined.)

Next, two models will be discussed in order to account for the strange behavior of V_8O_{15}. The first model runs into difficulties with the experimental facts outlined above. For this model, we assume that the specific-heat anomaly around 6.1 K is an ordinary

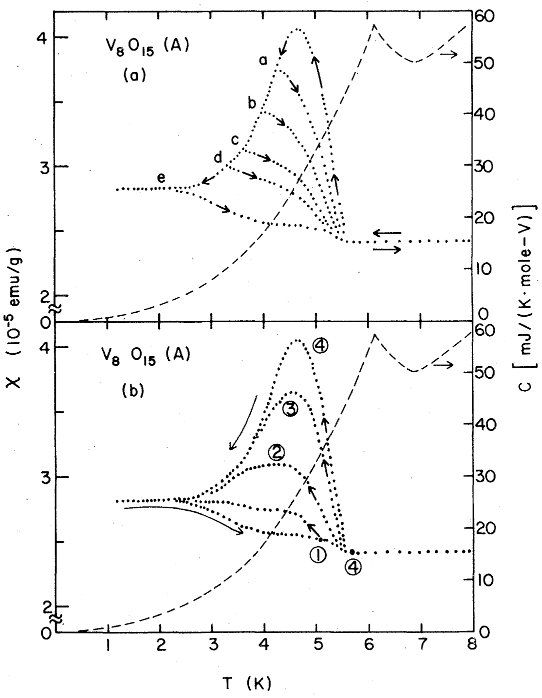

FIG. 7. Anomalous susceptibility of crystals from set *A*. The specific-heat data are shown in dashed curve for comparison. (a) First the sample is cooled and stopped at the position *a*; next it is heated. This process is indicated by arrows. The other loops from *b* to *e* indicate the same procedures. (b) The sample is cooled to 1.1 K, next heated to the position (1) and cooled again. The arrows show the direction of the temperature change. The other loops from (2) to (4) indicate the same procedures. All the curves are reproducible within the experimental precision.

antiferromagnetic transition due to localized magnetic moments, by analogy with other Magnéli phases. From the magnetic point of view, the small entropy change [0.03 J/(K mole-V)] indicates that singlet spin pairing is nearly complete for V_8O_{15} in this insulating phase since the fraction of vanadium ions having a magnetic moment is then of the order of 1 in 200. From this follows that V_8O_{15} is a very dilute magnetic system with a small average Curie constant. Therefore the temperature dependence of the susceptibility should be very small and is then undetectable within our experimental precision. However, the internal field estimated from the nuclear specific-heat contribution implies that half of the vanadium ions are subjected to a nuclear hyperfine field.[10] As this field must come from a magnetic moment of the vanadium ion, this disagrees with the result discussed above. It is also unnatural that no anomaly in the susceptibility was observed around 6.1 K. On the other hand, the magnetic susceptibility below 5.6 K might come from effects of impurities,[27] or crystal imperfections. Another possibility is a kind of magnetic domain structure, e.g., a canted antiferromagnetic structure could be postulated to explain the strange behavior in the susceptibility. It might also be speculated that the pairing energy is small and the transition to the antiferromagnetic state destroys the singlet spin pairing. The strong piece of evidence against this last idea comes from the specific heat. In that case, the excess entropy near T_N would be of the order of $R\ \ln(2S+1)$ and such a large value is not found. Another difficulty is that pair breaking was not found below T_N in NMR experiments[8,9] for other Magnéli phases which have higher T_N.

A quite different interpretation will be discussed now. As shown in Table I, the Néel temperature of V_nO_{2n-1} decreases to zero as the average number of *d* electrons decreases from two in V_2O_3 to one in VO_2. The properties of V_7O_{13} are quite different from the other Magnéli phases as it is metallic at all temperatures and this suggests that the properties of V_8O_{15} in the insulating phase can be different from the other Magnéli phases with $n \leq 6$.

The insulating state of V_8O_{15} may be viewed as a charge-density wave (CDW) state. There are two indications which can be related to CDW mechanism in vanadium oxides. First Colella *et al.*[28] found sharp anomalous peaks in Cr-doped V_2O_3 above 100 °C and pointed out that it might be due to structural perturbances by a CDW. Second, Gossard *et al.*[8] already speculated about the existence of CDW in V_4O_7 in the insulating state. In addition, they found a temperature-dependent exchange parameter J between spins S_i and S_j of the 4+-4+ pairs, which might be a kind of order parameter. A CDW can lead to a temperature-dependent shortening of the bond between vanadium ions by screening the electric field and so to the temperature dependence of J. However, the susceptibility in the insulating phase of V_4O_7 is not constant as it is for V_8O_{15}, so that the effect of the CDW must be less complete in V_4O_7 as compared to V_8O_{15}.

The detailed analysis about spin-density wave (SDW) and CDW by Overhauser[29,30] gives an electronic ground state for which the spin-up and spin-down electron densities are

$$\rho^+(\vec{r}) = \tfrac{1}{2}\rho_0[1 + p\cos(\vec{Q}\cdot\vec{r}+\phi)] \ ,$$

$$\rho^-(\vec{r}) = \tfrac{1}{2}\rho_0[1 + p\cos(\vec{Q}\cdot\vec{r}-\phi)] \ .$$

The mean electron density is ρ_0, the fractional modulation is p, and the wave vector is $\vec{Q}$. The three possible types of exchange instability are

$$\phi = 0$$

for pure CDW;

$$\phi = \tfrac{1}{2}\pi$$

for pure SDW;

$$0 < \phi < \tfrac{1}{2}\pi$$

for mixed CDW-SDW.

In the Hartree-Fock approximation the SDW and CDW states are degenerate and have lower energies than the plane-wave state. The degeneracy is removed by correlation energy corrections.

Suppose that for V_8O_{15} the metal-insulator transition at 68 K arises from effects of a CDW instability of the Fermi surface so that the system becomes an insulator with an energy gap. In addition, below 6.1 K the pure CDW state changes into a mixed CDW-SDW state. As the temperature is lowered, the phase difference 2ϕ would increase from zero to a finite, probably small, value so as to minimize self-consistently the free energy of the system. This phase difference between the spin-up and spin-down electron densities induces a magnetic moment on the vanadium ions.

The temperature-independent susceptibility between 5.6 and 68 K can be accounted for by a CDW state, since the charge densities for up-spin and down-spin waves are modulated in phase, so that this state does not have a spin polarization. The very small entropy change below 6.1 K can be understood on the basis of a SDW mechanism. The entropy change below 6.1 K arises from the energy used to eliminate the phase difference between the up-spin and down-spin wave. The collectively induced moment has no spin degree of freedom, and therefore, the entropy change is small in comparison with an individual localized moment system.

From the magnetic point of view the situation is similar to the SDW state in metallic chromium[31] in which the chromium ions have a self-consistently induced moment below the SDW transition and do not have a localized spin moment above this temperature. The observed entropy change in chromium is also small [0.018 J/(K mole-Cr)],[32] but comes from truncation of the Fermi surface by the energy gap of the SDW exchange potential.

The low-temperature anomalous behavior of the susceptibility can be a consequence of domain structure in the SDW state. A whole number of half wavelengths have to fit each domain so that the length of a domain is $(\frac{1}{2}\lambda)N$, where λ is the wavelength of the SDW and N is an integer. If N is even, the effective magnetic moment of the domain is zero. On the other hand, if N is odd, there will be a half a wavelength of uncompensated spins, so that this domain will contribute to the magnetization. Then the effective moment for the bulk property will be approximately proportional to ϕ/N. However just below the transition of 6.1 K the number of domains with effective up spin should equal the number with effective down spin. This would explain why the onset of the anomalous susceptibility occurs about half a degree below the maximum temperature in the specific heat. On further cooling interactions between the domains will tend to align the effective moments of the domains, and together with the increase in the magnitude of the phase shift account for the rapid increase of the magnetization. On still further cooling, it becomes energetically more favorable to let domains coalesce, and consequently N increases and the effective moment, ϕ/N, decreases. Once cooled to the lowest temperature the sample contains a few domains with a small magnetization, and on heating only the phase shift decreases, so that the magnetization changes a very small amount. The bulk magnetic properties for such a multidomain sample will depend critically on the domain structure and can change from sample to sample.

This model can explain qualitatively the nuclear specific heat. The induced electron-spin moment will produce a hyperfine field acting on the vanadium nuclei. Furthermore the local-electron density around each vanadium ion and the displacement of ions from their positions in absence of CDW-SDW will change the electric-field gradients. This leads to hyperfine splitting via the interaction of the nuclear quadrupole moment with the local electric field.

The combination of a CDW and SDW has not been observed before and it would be interesting if other experiments could verify this model. In addition, it will be necessary to clarify the mechanism responsible for the phase shift between spin-up and spin-down electron densities in an insulator.

IV. CONCLUDING REMARKS

The low-temperature susceptibilities of vanadium Magnéli phases V_nO_{2n-1} have been measured. The characteristic features of the susceptibilities are affected by the value of n. A large short-range-order effect was observed in V_3O_5. For V_4O_7 and V_6O_{11} the results of the susceptibilities do not support the magnetic linear-chain model as was already discussed by Khattak *et al.*[10] The average magnetic moments per vanadium ion are small in the insulating phases V_4O_7 and V_6O_{11}, which is a consequence of singlet pairing effect. For V_8O_{15} some remarkable features were observed in the susceptibility and the specific heat. If the transition of V_8O_{15} at 6.1 K is assumed to be an antiferromagnetic transition due to the remaining localized moments, by analogy with other Magnéli phases, then the small value of the magnetic entropy change indicates that the singlet pairing effect is extremely large and only $\frac{1}{200}$ of vanadium ions have a magnetic moment. This small fraction can explain the very small temperature dependence in χ above T_N; however it is in disagreement with the nuclear contribution to the specific heat below 1 K which indicates that half of the vanadium ions have a magnetic moment. Below 5.6 K the susceptibility is sample dependent, and some crystals show irreversible anomalies. This mechanism is not sufficiently understood at present. Besides the effects of impurities and crystal imperfections, another possibility is discussed from the point of view of a mixed CDW-SDW mechanism.

ACKNOWLEDGMENTS

The authors would like to thank Professor A. W. Overhauser for valuable discussions and helpful comments on the manuscript. It is a pleasure to acknowledge his encouragement and enlightment throughout the course of this study. The authors are indebted to B. F. Griffing for kindly supplying us with his specific-heat data on V_3O_5 before publication. We are grateful to Professor W. R. Robinson and Professor R. Colella for x-ray analysis, and professor H. Sato and Professor J. M. Honig for stimulating discussions. This work was supported by NSF Grant No. 76-80551 and NSF-MRL Program No. DMR 77-23798.

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