JOURNAL OF SOLID STATE CHEMISTRY 12, 376–382 (1975)

Insulator–Metal Transitions: Recent Experimental Results*

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Received July 3, 1974

Experimental results relating to insulator–metal transition problems in V_2O_3, VO_2, Ti_4O_7, and NiS are reviewed. The controversial nature of the high temperature Mott transition in V_2O_3 is commented upon. The pairing interaction in VO_2 and Ti_4O_7 is shown to be one of the important features in such transitions. The itinerant nature of conduction electrons in NiS in the ground state is shown to have been established.

I. Introduction

In recent years a great number of new experimental results pertaining to the insulator–metal transitions on single crystals of vanadium and titanium oxides, as well as transition metal sulfides has been published. An excellent and exhaustive earlier review of the subject (*1*) already exists and no attempt will be made here to cover the entire recent literatures on the subject.

We have chosen to cover some of the results obtained recently in the following four systems: (1) V_2O_3, (2) VO_2, (3) Ti_4O_7, and (4) NiS. Although a great deal of recent work has been done on Ti_2O_3 (*2*), as well as on one-dimensional systems (*3*), we have decided not to include them in this short review. We have also not covered the tungsten bronzes, metal–ammonia solution, transitions in dense mercury vapor, as well as the rare earth chalcogenides. The recent review of Mott (*4*) covers some of these topics.

II. Experimental Results

A. V_2O_3

Of all the transition metal oxides, the most extensively studied in recent years has been V_2O_3, to a large extent by McWhan and coworkers (*5*). Pure V_2O_3 is monoclinic and an antiferromagnetic insulator at $T = 0$, with 1.2 μ_B/V atom (seemingly only one of the two $3d$ electrons of V^{3+} contributing to sublattice magnetization). At 150°K, the A.F.I. phase becomes metallic, with a dramatic rise of conductivity by over six orders of magnitude, and accompanied with a structural transition to α-corundum. This transition is first order with sharp specific heat anomaly and the metallic phase shows a Pauli susceptibility, although, with an apparent Curie–Weiss temperature dependence, considered characteristic of highly correlated electrons moving in a narrow band. Both pure V_2O_3, as well as V_2O_3 doped with Cr (or Zr), show a second transition at a still higher temperature, that has been characterized by McWhan and collaborators as a *Mott transition*, at which the metallic phase reverts to a localized insulating phase due to Mott–Hubbard correlation. If it is a Mott transition, it is the only known example of it, although the higher temperature phase is insulating rather than metallic, contrary to Mott's original hypothesis. Some of the evidence supporting the Mott transition is as follows.

(a) With Cr addition, c/a the ratio, as well as volume shows a discontinuous change showing no doubt that a first order phase transition with a parameter change but

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* Invited paper.

Printed in Great Britain

without change of lattice symmetry is occurring. For a given Cr concentration, increasing temperature has the same effect. The lattice parameter changes of pure V_2O_3 are found to be anomalous around 500–600°K.

(b) This lattice parameter transition is accompanied by a jump in resistivity and the less dense phase at the higher temperature seems to show a negative temperature coefficient of resistivity characteristic of an insulator.

(c) For pure V_2O_3, a shallow relative maximum occurs in magnetic susceptibility between 400 and 550°K. This maximum moves to lower temperature and becomes more pronounced with increasing Cr content. This susceptibility can be fitted to Curie–Weiss behavior, with 2.69 μ_B/V atom, compared to 2.37 μ_B in the metallic phase, indicating a greater degree of *d* electron localization.

(d) The recent NMR measurements of Jerome et al. (*6*) show that, in the metallic phase, the nuclear relaxation rate $1/T_1$ in pure V_2O_3 obeys a Korringa relationship (i.e., relaxation rate proportional to temperature, characteristic of hyperfine interaction with itinerant electrons) while near 500°K and above, $1/T_1$ is found temperature independent, characteristic of nuclear spin relaxation through interaction with localized *d* electrons.

(e) The resultant phase diagram exhibits a critical point, above which the high temperature transition is expected to be continuous. Pure V_2O_3, being above the critical point undergoes the Mott transition in a continuous manner.

More recently, Honig (*7*) and co-workers have challenged the validity of the high-temperature transition as being a Mott transition, and they seriously question some of the experimental data on the basis of which the phase diagram of McWhan et al. (*5*) was constructed. The data of Honig and co-workers (*7*) show (see the article by Honig in this conference):

(a) There is no critical point. Even for pure V_2O_3, phase separation and a substantial two phase region exists up to as high as 700°K in complete disagreement with X-ray results by Jayaraman et al. (*8*).

(b) The resistivity increase at the transition is a spurious metallurgical effect, probably due to internal grain boundaries in a highly heterogeneous two phase region. The effect depends on the scanning rate and the less dense phase actually reverts back to a metallic domain at ~800°K. The Seebeck coefficient does not support the higher temperature phase as being a Mott insulator either. These authors identify this phase transition as an allotrophic metal to metal phase transition.

These are serious objections. Lack of measurable specific heat anomaly at the phase transition for the Cr-doped samples only helps to compound the controversy (the two phase region extends over a broad temperature range, due to sluggish metallurgical kinetics and the internal energy difference of the two phases is probably small, as seen by the almost vertical *dTc/dp* curve of McWhan et al. (*31*)). A critical reexamination of all the nontransport data supporting the Mott transition argument in V_2O_3 system is certainly very desirable. The Curie–Weiss behavior of the higher temperature phase does not guarantee the existence of local moment on V atoms (many metallic systems like Pd, (*9*) $HfZn_2$, or for that matter V_2O_3 above 150°K show temperature-dependent susceptibility). Nor does the temperature independence of $1/T_1$ establish the local moment regime. There are both theoretical (Doniach, Morriyo) and experimental situations (in MnSi || for $200 < T < 300$°K) in metals where nuclear spin relaxation rate is temperature independent. Also if the Fermi temperature is low in V_2O_3 (as had been proposed by Rubinstein (*12*)), then for $T > T_F$, $1/T_1$ would tend to be temperature independent. No excessive electron localization is indicated by the value of the magnetic moment/V atom up to ~4% Cr, in Menth's (*13*) data (see his Fig. 6, ~2.5 μ_B/V atom), although in the same region the electrical resistivity, at room temperature, goes up with Cr addition by several orders of magnitude. The isomer shift data of Wertheim et al. of both pure V_2O_3 as well as Cr-doped samples, on the other hand make a very strong case for electron localization and hence a Mott-type transition. It is intuitively evident that the higher Cr-doped samples would be insulating (Cr_2O_3 is insulating) and that at some Cr concentration Mott–Anderson localization due to random lattice may set in. But whether there exists a pure Mott transition in V_2O_3, first order in concentration or with temperature, remains to be clarified.

B. VO₂

The other member of the vanadium oxide family, that shows an enormous transition in conductivity at 340°K, in which the structure changes from a low temperature insulating monoclinic phase to the higher temperature metallic rutile phase is VO_2 (*14*). Due to intensive recent work on this system, first by Marezio et al. (*15*), then by Hagenmuller et al. (*16*), and Launois et al. (*17*), one encounters a less controversial idea about this system and that will be summarized briefly. Using Cr or Al as a dopant, one finds that beside the insulating monoclinic phase M_1, one goes into with as little as 0.1 % Cr, at temperatures below 340°K a second monoclinic phase M_2, which is also insulating. At intermediate temperatures, a third insulating phase, called the T transition structure also appears (Fig. 1 shows the phase diagrams with Al) (*18*).

In the insulating M_1 phase, with or without Cr, the near-neighbor V atoms (V^{4+}, $3d^1$) pair into a diamagnetic singlet state (they also twist out of plane, due to a local antiferroelectric distortion, giving rise to a zigzag chains, Fig. 2). With further Cr or Al addition the M_2 insulating phase appears in which the V atoms are paired but not twisted, but on the other set the V atoms remain twisted but not paired, essentially as free $3d^1$ spins. Launois et al. (*17*) were able to confirm, by observation of two distinct V^{51} NMR lines, that one line corresponds to that of pure insulating VO_2 (characteristic of a bonded V–V pair), while the other line is characterized by a negative knight shift and by a large line width as expected for a site with a localized d electron in an insulator. In the transitional phase T, that occurs at lower temperature, progressive dimerization of the Heisenberg linear chain of M_2 occurs, until at the lowest temperature, no distinction exists between T and M_1. This clearly implies that the $3d$ electrons of V atoms are on the localized side of the Mott transition, and that a substantial part of the energy gap in the insulating phases of VO_2 may be ascribed to a correlation Mott–Hubbard gap. For the Cr-doped samples in the M_2 phase, the free V spins on the one-set of chains give rise to an extra contribution to magnetic susceptibility above $T >$ 100°K, that fits a linear-chain Heisenberg model.

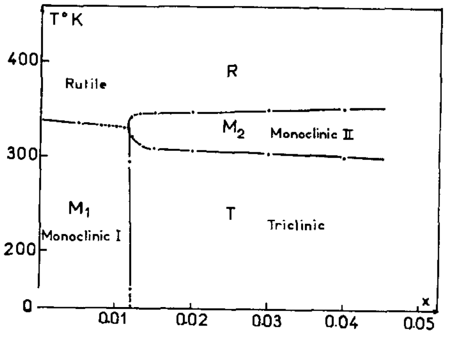

FIG. 1. Phase diagram VO_2–Al system ($V_{1-x}Al_xO_2$).

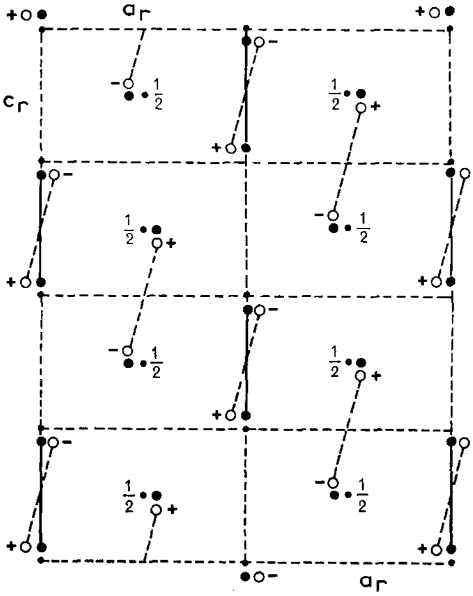

FIG. 2. Pairing and distortion in VO_2 (V positions). Solid lines pairs in M_1 phase; dotted lines pairs in M_2 phase; simple dots V position in undistorted rutile.

These recent experiments on pure and doped VO_2 point out that no band model is needed to explain the insulating state (the electrons here are localized or paired). The recently proposed band models (*19*) conceive of the energy gap of the M_1 phase, to a bonding and antibonding splitting of the V–V pairs. In the case of a one-dimensional chain, with Hubbard term U, and hopping term t, the lowest eigen value with energy $t = 1/2U - (4t^2 + 1/4U^2)^{\frac{1}{2}}$, is a singlet. In the band limit ($t \gg U$), the energy gap to the first excited state is $2|t|$, while in the localized limit ($t \ll U$), there is a triplet of states (magnetic states) with energy $4t^2/U$ above the singlet (the charge carrier excitation states are an energy U above). That indeed one is close to the localized regime, is dramatically shown, in Fig. 3, in the Mössbauer spectrum of Sn-doped VO_2 (*20*), where breaking of a V–V pair induces a local magnetic alignment of the surrounding spins, which shows up as a hyperfine field splitting in otherwise diamagnetic VO_2. One can indeed state that a paired singlet state is very close to being an antiferromagnetic state. One should finally add that there is still considerable uncertainty about the respective roles played by pairing and antiferroelectric distortion in stabilizing the localized state.

C. Ti_4O_7

The importance of the charge localization due to pairing is again illustrated in the insulator–metal transition in Ti_4O_7. It belongs to the family of Magnéli phase (M_nO_{2n-1}), is triclinic, and contains two types of Ti chains, running parallel to the pseudo rutile C-axis. Ti_4O_7 exhibits two electrical transitions (*21*), the first a semiconductor–semiconductor transition at 130°K, and the second a semiconductor–metal transition at 150°K. The magnetic susceptibility (*22*) is temperature independent, of Van Vleck type below 150°K, shows a sharp enhancement at 150°K, and is Pauli paramagnetic above this temperature. There is no anomaly of magnetic susceptibility at the 130°K transition. Marezio et al. (*23*) showed that below 130°K, the Ti chains consist of either Ti^{3+} ($3d^1$) or of Ti^{4+}($3d^0$) and that the 3^+ sites are paired to form the diamagnetic singlet (Figs. 4a and 4b). Above 150°K, the average charge is 3.5+, with the extra electron itinerant over all Ti sites.

Recently Schlenker et al. (*24*) have performed extensive specific heat, susceptibility and EPR measurements on Ti_4O_7

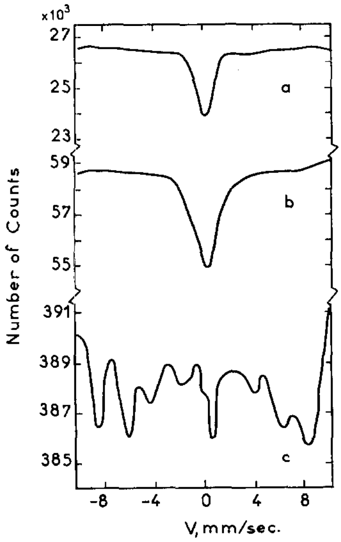

FIG. 3. Mössbauer spectra Sn-doped VO_2. (a) at 353°K above T_t; (b) at 313°K; (c) at 77°K below T_t.

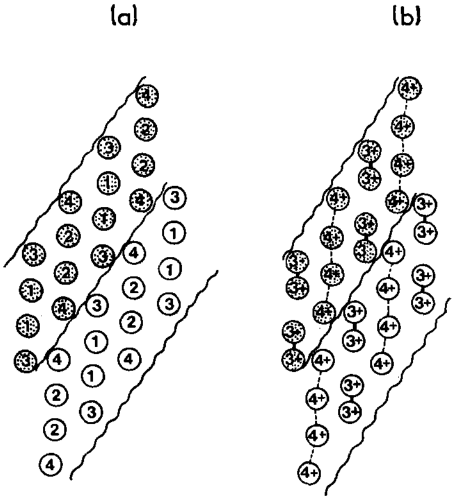

FIG. 4. Pairing interaction in Ti_4O_7 (a) $T > 150°K$ (b) $T < 130°K$.

single crystals. Their specific heat data shows convincingly that the 130–150°K intermediate phase is well described by a configuration, wherein the Ti^{3+}–Ti^{3+} pair chains no longer alternate with the Ti^{4+} chain, as in the low temperature phase, without any long-range order. Anderson (*25*) discussed such a phase as a 'classical liquid of pair bonds.' The entropy of the 130°K transition, 0.70 cal/mole fits the configuration change. The high-temperature transition is essentially due to the disappearance of the charge excitation gap, and the total entropy change of 3.40 cal/mole °K is due only partly to electronic entropy (1.50 cal/mole °K), the rest deriving entirely from the lattice transition.

Pairing interaction analogous to Ti_4O_7, exists also in the Magnéli phase of vanadium, V_4O_7, as studied recently by NMR by Gossard et al. (*26*) V_4O_7 is metallic above 250°K, and is insulating below; a peak in magnetic susceptibility which is not well understood, occurs at 40°K. Structural pairing below 250°K gives rise to V^{3+}–V^{3+} and V^{4+}–V^{4+} pairs, involving three-quarters of atomic sites, leaving a set of free V^{4+} spins ($3d^1$) localized. It is conceivable that these free spins order antiferromagnetically at 40°K. Both the EPR results of Schlenker et al. (*27*) on the broken pairs in Ti_4O_7 and NMR results of Gossard on V_4O_7, show the importance of the spin relaxation mechanism, due to charge excitation (occasional double occupancy of the resonating site) in these systems.

D. NiS

Hexagonal NiS exhibits a metal–nonmetal transition, which has aroused considerable interest since the first systematic study due to Sparks and Komoto (*28*, *29*). The principal experimental result shows a first order transition, from an antiferromagnetic state to a more conducting state with a temperature independent Pauli susceptibility, and an abrupt volume contraction of about 1.9% without symmetry change—the sublattice moment 1.8 μ_B/atom for the most stoichiometric samples vanishes at the transition temperature ~265°K. The transition temperature is very sensitive to stoichiometry and external pressure (*30*, *31*). There has been speculations whether this transition is (a) a Slater transition due to doubling of the lattice periodicity below T_t, due to antiferromagnetic lattice formation; (b) a transition from an antiferromagnet with local moments to a delocalized *d*-band metal, without moments, hence a Mott transition; (c) a transition from an itinerant band antiferromagnet to a delocalized *d*-band metal without moments.

The first speculation can be eliminated, since the real lattice periodicity in NiS is never doubled, but remains same due to the positions of the sulphur atoms in the unit cell. The recent detailed experimental work of Coey and collaborators (*32*, *33*) involving specific heat, Mössbauer and neutron measurements have also established that the Ni-moments in the ground state of NiS are not localized, but are itinerant. This eliminates the second speculation; one is thus left with the third possibility as a sound working hypothesis pertaining to the NiS transition. The evidence that NiS is an itinerant antiferromagnet at $T = 0$, are the following.

(1) The work of Koehler and White (*34*), as well as that of Townsend et al. (*35*), show convincingly that the electrical conductivity is substantially temperature independent below T_t, and is probably semimetallic. Of course this evidence is insufficient because the conduction electrons are not necessarily the magnetic electrons.

(2) Both $\chi_\perp$ and $\chi_\parallel$ are remarkably temperature independent (unlike any conventional antiferromagnetic) and on a standard local moment model extrapolates to Tn ~ 1600°K. However, the Mössbauer hyperfine field (*36*), extrapolates to $T_n \sim 400$°K, if local moments are assumed. The discrepancy between these two sets of results vanishes if the moments are assumed to be itinerant.

(3) Measurement by neutrons of the magnetic moments on Ni for $Ni_{1-\delta}S$ (where δ is the vacancy concentr. on the nickel sites) shows an extremely strong dependence of μ on δ (Fig. 5), which is difficult to reconcile with localized moments; there is an abrupt decrease of *C*-axis near $\delta = 0.03$, at 4.2°K, with loss of moments, and a transition to the metallic state.

(4) Finally, the low-temperature heat

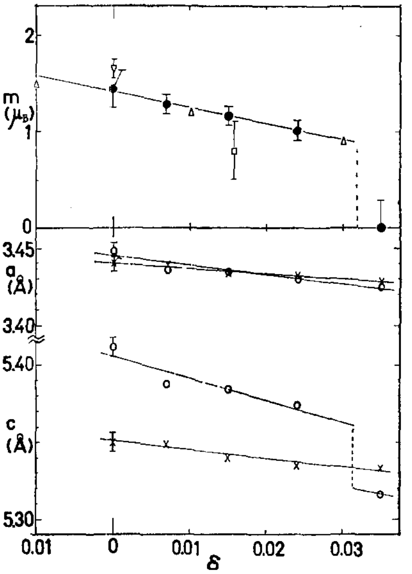

FIG. 5. Magnetic moment m and lattice parameter in NiS, as an *fn* of Ni vacancies δ at room temperature.

capacity (Fig. 6) clearly shows a nonzero density of states, at the Fermi level, corresponding to 3.1 states/eV, that jumps to 7.7 states/eV at the transition, indicating a partial overlap of the two Hubbard bands at $T=0$ as postulated by Mott and White (*37*). Of the 5.32 J/mole K of the entropy of transition, only a third is of electronic origin, the rest deriving from the lattice—a fact buttressed by the pronounced drop in the recoilless Mössbauer factor f (*38*), at the transition.

In summary, NiS offers an extremely attractive system for model theoretical calculations of nonmetal–metal transition, given the host of precise data now available, and the relatively simple symmetry of the lattice.

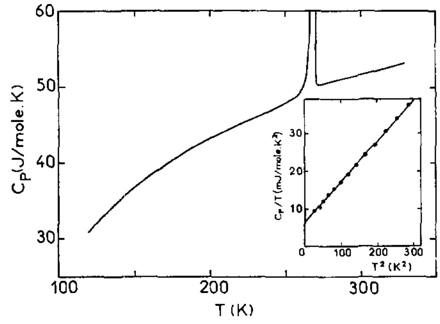

FIG. 6. Low temperature lattice *sp* heat in NiS.

Acknowledgments

The author wishes to thank J. M. D. Coey, C. Schlenker, and C. Villeneuve for making available their data before publication.

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