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METAL-INSULATOR PHASE TRANSITION IN VO₂

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Résumé. — On passe en revue les effets d’alliages et de comportement sous contrainte uniaxiale des propriétés structurelles et magnétiques de VO₂.
De cela on déduit que les corrélations entre électrons sont importantes : (i) dans la phase métallique, à partir des résultats obtenus dans les alliages V₁₋ₓNbₓO₂, (ii) dans les phases isolantes de VO₂ pur à pression ambiant (M₁), sous contrainte uniaxiale ou en présence d’impuretés de Cr (T et M₂).

Abstract. — The effects of doping and uniaxial stress on the structural and magnetic properties of VO₂ are reviewed. Important electron-electron correlation effects are deduced: (i) in the metallic phase from the results obtained in V₁₋ₓNbₓO₂ alloys, (ii) in the insulating phases of pure VO₂ at ambient pressure (M₁), under uniaxial stress or in the presence of Cr impurities (T and M₂).

Discovered in 1959 by Morin [1], VO₂ undergoes a first order metal-insulator phase transition at 340 K from a high temperature rutile phase (R) to a low temperature monoclinic phase (M₁). The first experiments showed the absence of any magnetic ordering [2] and the presence of V-V pairing, suggesting a one electron description of the insulating phase; the band gap being induced by the crystallographic distortion forming the pairs (Adler et al. [3] Goodenough [4]).

Describing the metallic phase in term of a simple band theory, Berglund and Guggenheim [5] proposed that most of the large entropy change (ΔS = 1.5 k/VO₂ unit) coming from lattice vibrations, stabilizes the metallic phase. A phonon softening mechanism due to strong d electron-phonon interactions was proposed by Paul [6] and Hearn [7]. On the other hand, following an idea put forward some years ago by Goodenough [8], Rice et al. [9] suggested that each cationic electron gets trapped in bonded singlet V-V pairs forming the insulating phase. (They also calculated that, even in the atomic limit, the energy of such a phase can compare favorably with that of a Mott insulator in its antiferromagnetic state.) Considering also the strong similarities (electrical conductivity, magnetic susceptibility) between properties of the metallic phases of VO₂ and V₂O₅, they proposed a unified description of the two phases in terms of a strongly correlated or exchange enhanced metal. In such a description, a sizeable contribution to the entropy change at the metal-insulator transition comes from the electrons.

This controversy needed a much more detailed study of VO₂. A fruitful way was opened by the study of the effects of various dopants on the metal-insulator transition. In this paper we present in the first part the phase diagrams of the two classes of impurities (Nb and Cr classes) and their relation to that of pure VO₂.

In the second part we discuss the metallic phase, using mainly the V₁₋ₓNbₓO₂ system. The properties of the insulating phases, of VO₂ under uniaxial stress and of the V₁₋ₓCrₓO₂ system, are presented in the third part. The last section discusses the problem of the metal-insulator phase transition in VO₂.

1. The phase diagram of VO₂ and its alloys. — In its high temperature phase VO₂, has a rutile (R) structure (Fig. 1) composed of two equivalent vanadium atoms A (center) and B (corner) per cell; each V atom being surrounded by an oxygen octahedron whose axis point in the (110)ₘ and (110)ₘ directions for the A and B vanadium atoms, respectively.

![Fig. 1. Rutile cell of the high-temperature phase of VO₂. Distances, in angstrom, are taken from reference [10].](http://dx.doi.org/10.1051/jphyscol:1976408)
monoclinic insulating phase \((M_1)\) can be presented as the result of a two components distortion: a pairing of V atoms along the \((001)_b\) axis and a zig zag (or antiferroelectric) distortion along the octahedron axis \([4]\). Due to this distortion all the vanadium atoms belong to equivalent V-V pairs slightly tilted from the \((001)_b\) axis, as schematically shown in figure 2a.

![Figure 2a](image)

**Figure 2.** - a) The phase diagram of \(V_{1-x}Cr_xO_2\) alloys (after ref. \([13]\)). In each insulating phase, vanadium chains of the A and B sublattices, contained in the \((110)_h\) and \((110)_h\) planes respectively, are represented. The arrows in the T phase indicate the displacement of the V atoms when the temperature increases. b) The phase diagram of pure VO\(_2\) vs temperature and stress. After reference \([18]\).

Figure 2a presents the phase diagram of the \(V_{1-x}Cr_xO_2\) system. For only few thousands of chromium atoms two new insulating phases \(M_2\) and T are stabilized between the R and \(M_1\) phases. The simplest way to understand these phases is to view the rutile phase as two interpenetrating sublattices A and B of V chains parallel to the \((001)_b\) axis; each type of sublattice consists either of A vanadium atoms or of B vanadium atoms as previously mentioned. In the monoclinic \(M_2\) phase, Marezio et al. \([11]\) have shown that the V atoms of the A sublattice are strongly paired along the \((001)_b\) axis while the V atoms of the B sublattice form zig zag chains along the same direction, as shown schematically in figure 2a. Because of the interaction between the two vanadium sublattices via oxygen atoms, the pairing in A sublattice causes the zig zag (or antiferroelectric) distortion in B sublattice, giving rise to two inequivalent sublattices, each exhibiting half of the distortion of \(M_1\). This consequence of the rutile structure shows that, contrary to Goddenough suggestion \([4]\), the two components of the crystallographic distortion of VO\(_2\), cannot be separated by atomic substitutions. Electric field gradient (E. F. G.) measurements show that the T phase corresponds to a progressive dimerization of the zig zag chains in the B sublattice and a progressive tilting of the V pairs in the A sublattice leading to the two equivalent V sublattices in the \(M_1\) phase (Fig. 2a) \([12]\). X ray structural determination \([12, 13]\) gives a triclinic symmetry for this transitional phase T. This type of phase diagram is also found with others impurities like Al \([14]\), Fe \([15, 16]\) oxidizing the \(V^{4+}\) state to the \(V^{5+}\) state in the \(M_1\) phase.

The exact mechanism by which a particular group of impurities can stabilize T and \(M_2\) and break the symmetry between sublattices A and B is not yet clear (migration of holes \((V^{5+}\) sites), to the B sublattice, which compensate the trivalent ions \((Cr^{3+}\) for example) of the A sublattice has been suggested \([12, 17]\). The break in the symmetry has been done more directly by applying a uniaxial stress in the \((110)_h\) direction in pure VO\(_2\) \([18]\). The phase diagram thus obtained is presented in figure 2b. This experiment proves that the new insulating phases T and \(M_2\) are alternative phases of pure VO\(_2\). Figure 2b shows also unambiguously that the critical stress, \(S_c \sim 100-300\) bars, for which the \(M_2\) phase appears is so small that the free energy of \(M_1\) and \(M_2\) are extremely close at temperatures just below the metallic rutile phase in pure VO\(_2\).
Reyes et al. [19] have recently claimed that the T phase might be a mixed phase region between $M_1$ and $M_2$. In fact macroscopic studies (X ray diffraction [11] [16-20]), as well as microscopic studies (Nuclear Magnetic Resonance (N. M. R.) study of the quadrupolar effects on more nuclear transitions than just the central one [12, 21] and Electronic Paramagnetic Resonance (E. P. R.) observation of $Cr^{3+}$ and $V^{4+}$ centers [17]) demonstrate that there is a big difference in the symmetry of $M_1$ and $M_2$ phases, and that a third symmetry is presented by the T phase. The conclusion of Reyes et al. is related to their limited observation of the $(-\frac{1}{2}, +\frac{1}{2})$ nuclear transition only, for which the effects are not clearly separated, and to their ignorance of the earlier measurements on the quadrupolar N. M. R. satellites, E. P. R. and X ray work.

A mixed phase region can in principle occur at each first order transition if the Cr atoms are free to migrate and form two coexisting phases, one Cr rich and the other Cr poor. However the temperature of interest here are too low for such a migration to play any role and no mixed phase has been observed in a few degree temperature range near the first order T-$M_2$ and $M_2$-$R$ phase transitions [12, 16, 22]. In some of the samples a broadening of the $M_1$-T transition (where no measurable latent heat had been reported [12, 16]) was observed. Because of the large variation of the $M_1$-T transition temperature with impurity concentration, sample inhomogeneities might yield to such broadening. In addition, such mixing effects couldn’t arise in VO$_2$ under uniaxial stress.

Figure 3 presents the phase diagram, determined by Villeneuve et al. [20, 23] for the $V_{1-x}Nb_xO_2$ system. At low impurity concentration, the insulating phase $M_1$ is destabilized with respect to the metallic one; no new phase is observed. This type of phase diagram is typical of impurities like Nb [23], Mo [24], W [25], Re [26], F [27] reducing the V$^{4+}$ state to the V$^{3+}$ state in the insulating phase $M_1$. In this phase the impurities break the pairs and create one V$^{3+}$ ion in the Nb case [28] or two V$^{3+}$ ions in the W case [29], giving rise to Curie Weiss contribution to the magnetic susceptibility. Such V$^{3+}$ ions have been studied by E. P. R. in the niobium alloys [30]. It is interesting to note, as remarked by Nygren [31], that the above alloys present, in the low concentration limit, a linear decrease of the metal insulator transition temperature of $12\sigma \pm 1$ percent of V$^{3+}$ ions. Such a decrease, proportional to the number of V$^{3+}$ created, suggests that the pair breaking is the main mechanism to destabilize the insulating phase [32]. Such a V$^{3+}$ state, appearing with so different impurities (as well as the V$^{3+}$ state found with Cr [12], Al, Fe impurities) is difficult to understand in the framework of a pure band model for the $M_1$ phase. On the other hand, the V$^{3+}$ or V$^{3+}$ state formation is explained easily by electronic transfer in a singlet bond molecular picture of the insulating phase of VO$_2$ [9], [32].

Figure 3 shows that the structure of the low temperature region, obtained by usual X ray methods, change from monoclinic $M_1$ to a pseudo monoclinic $M'$ and then to a pseudo rutile $R'$ when the niobium doping increases. Comes et al. [33], using X ray diffuse scattering have shown that the above pseudo structures can be explained by an average of disordered $(110)$ and $(110)$ planes containing V-V pairs of atoms A and B respectively (an average on one type of planes giving $M'$ [34] and an average on both type of planes giving $R'$ [33]). In the $M'$ and $R'$ pseudo phases, the local order remains of $M_1$ type. X Ray diffuse scattering [33] also shows that the high temperature rutile (R) structure is not changed by niobium alloying. By alloying, the conservation of the rutile symmetry in the high temperature phase, allows a meaningful study of the effects of Nb doping on the metallic phase, even in the higher concentrations.

2. The high temperature rutile phase. — VO$_2$ in its metallic phase is a poor metal with resistivity of the order of $10^{-4}$ $(\Omega \cdot cm)^{-1}$ [6] which is comparable to that of V$_2$O$_3$ [9]. The spin susceptibility deduced from the plot of $^{51}$V NMR Knight shift versus magnetic susceptibility (Fig. 7) leads to a value of $\chi_d \sim 6.2 \times 10^{-4}$ emu/mole V at 370 K. The deduction of this value from more detailed NMR data given in reference [28] is presented in the appendix. This value of $\chi_d$ is only 25 $\%$ lower than the spin susceptibility of V$_2$O$_3$ : $\chi_d \sim 8 \times 10^{-4}$ emu/mole V at 155 K [35]. The above comparison suggests a similar description for the metallic phases of the two compounds. In the VO$_2$ case, one can deduce, from the spin susceptibility, an effective density of states at the Fermi level : $\pi^*(E_F) = 10$ states/eV and spin direction. This enhanced value is in favor of quite important electron-electron interactions in the metallic phase of VO$_2$. Two different interpretations of this large spin susceptibility have been given. According to Mc Whan et al. [36], the enhanced susceptibility results mainly from spin fluctuations in a strongly correlated electron gas, following the theory of Brinkman and Rice [37]. On the other hand, Zylbersztejn and Mott [38] view the metallic VO$_2$ as similar to transition metals like Pt or Pd : electrons in a comparatively wide band ($\pi^*$) screening out the interaction between the electrons in a narrow overlapping band ($\sigma$) [39]. It is difficult from the study of pure VO$_2$ to differentiate clearly between the above models. Much more can be learnt from the study of the $V_{1-x}Nb_xO_2$ system in its high temperature rutile phase.

Introducing a Nb atom (iso electronic of V atom) in VO$_2$ leads to the following local effects (32) :.

- local repulsive on electron potential : $E_4 > E_3$,
- local attractive electron-electron interaction term : $U_4 < U_3$,
- local change in transfer integrals.
The Nb atom, which is bigger than the V atom, produces also a very big dilatation of the rutile cell: \( c_R \), \( a_R \) and the ratio \( c/a \) increase strongly with the Nb concentration [23].

In the case of \( V_{1-x}Nb_xO_2 \) alloys the magnetic susceptibility increases rapidly with increasing \( x \) [28]. This effect must be attributed to an increase in the d spin susceptibility. In the appendix we present more detailed \(^{51}\)V NMR data, which precisely shows that in the low niobium concentration limit \((x < 0.1)\) this increase in susceptibility seems spatially homogeneous, and presents no local effects around the niobium atoms. The fact that Nb impurities are almost entirely in the metallic state is quite unusual (by comparison with the Cr impurities in metallic VO\(_2\) which looks like \( \text{Cr}^{3+} \) with an increase in the magnetic susceptibility mainly localized around the impurity [12]). The absence of local effects might be due to the near cancellation between two opposite effects which are [32]:

a) a decrease in the local enhancement factor due to the defect in electron-electron interaction.

b) a local increase in the density of states resulting in an increase in the total density of states.

In the absence of important local effects, the increase in the magnetic susceptibility might be due to the strong dilatation of the lattice, produced by Nb alloying. Taking Goodenough’s one electron description of the metallic phase [39], an increase in the \( c_R \) and \( a_R \) lattice parameters will decrease the \( t_{\|} \) and \( \pi^* \) bandwidths and the increase of the \( c/a \) ratio will destabilize \( t_{\|} \) with respect to \( \pi^* \). Both effects, which are responsible for decreasing \( B \), will increase the Hubbard \( U/B \) ratio, that is to say that the importance of electron-electron energy correlation will increase with respect to electronic kinetic energy. In this description, as \( x \) increases the electronic gas will become more and more correlated [40].

Increasing the Nb concentration \( x \), the magnetic susceptibility increases and its temperature dependence becomes more and more Curie like (Fig. 4a). In the high temperature region \((T > 400 \text{ K})\), for \( x \approx 0.12-0.15 \), the associated Curie constant is of the order of 0.5-0.6 emu/mole K (Fig. 4b), larger than expected for a non degenerated electronic gas. This behaviour has to be confirmed by an extension of the susceptibility measurements at higher temperature. Nevertheless we would like to suggest that the large value of the Curie constant in the metallic phase could be due to the formation of clusters of moments (i.e. spin polaron formation in a highly correlated electronic gas; for reference see [41]). For these concentrations NMR measurements show a broadening of the \(^{51}\)V linewidth which is proportional to the magnetic field (see appendix). This broadening could be either due to local effects arising from the surroundings of Nb atoms or (and) to the presence of spin polaron. In the same Nb concentration range, the metallic conductivity decreases with increasing \( x \) and for \( x \approx 0.20 \) an electrical gap appears. So, in the same rutile structure, a progressive metal-insulator transition happens when the Nb concentration increases. In the insulating state two chemical formulas have been considered for the electronic configuration: (I) \( V^{3+}_xV^{4+}_{1-x}Nb^{5+}_xO_2 \) and (II) \( V^{3+}_xV^{4+}_{1-x}Nb^{5+}_xO_2 \). The value of the Curie constant in the limiting case of \( x = 0.5 \), see figure 4b and reference [43], and the change in the sign of the thermoelectric power for \( x \approx 0.33 \) [23] favors the first electronic configuration [32]. As Mott Hubbard correlations cause each atom to have an integer number of electrons, randomness is essential in bringing about a semiconducting state described by the formula \( V^{3+}_xV^{4+}_{1-x}V^{5+}_{1-2x}Nb^{5+}_xO_2 \). The metal insulator transition is certainly due to a mechanism combining disorder and correlation effects [32]. Starting with the above description of the metallic phase in which the cluster of spins begins to appear as the electronic gas becomes more and more correlated, one can think that the local effects around the niobium impurities will increase strongly when the local repulsive electron potential on the Nb site is comparable to that of the intraatomic repulsion \( U \) or the bandwidth \( B \). One can also expect an increase in the screening length with increasing \( x \).

The above effects would give rise to a transition from \((V^{4+}, Nb^{5+})\) to \((V^{3+}, Nb^{5+})\) configuration in which the spin polarons (clusters of magnetic moments around an excess of electron in a \( V^{3+} \) state) might be trapped electrostatically by an excess of hole on the

![Fig. 4. - a) Inverse susceptibility \( x^{-1} \) of the concentrated alloys \( V_{1-x}Nb_xO_2 \) vs temperature (after ref. [20] and [28]). b) High temperature Curie constants obtained from (a) vs Nb concentration. Solid lines correspond to chemical formulas \( V^{3+}_xV^{4+}_{1-x}V^{5+}_{1-2x}Nb^{5+}_xO_2 \) (I) and \( V^{3+}_xV^{4+}_{1-x}Nb^{5+}_xO_2 \) (II).](image)
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\textbf{C4-53}

\textbf{3. The low temperature insulating phases.} — The crystallographic relations among the M\textsubscript{1}, T, M\textsubscript{2} insulating phases, presented in the first part are shown schematically in figure 2a. We have also shown that the magnetic properties of the M\textsubscript{1} phase are strongly in favor of the V-V molecular description of this phase. What is the importance of correlations between electrons in the ground state of a pair? Is the description best in term of molecular or atomic orbitals? To answer this question we will start from the M\textsubscript{2} phase and, through the T phase, add the remaining cationic distortion to obtain finally the M\textsubscript{1} phase.

The M\textsubscript{2} phase consists of two different sublattices A and B of vanadium atoms. In the A sublattice chemical shifts measurements show that strongly paired V atoms exhibit only a measurable orbital contribution to the magnetism like in the M\textsubscript{1} phase [12, 45]. On the contrary the NMR shift measurements show that the equispaced V atoms forming zig zag chains in the B sublattices exhibit a strong spin susceptibility ($\delta\chi \approx 2 \times 10^{-4}$ emu/mole V) giving rise to the increase in the magnetic susceptibility observed in the M\textsubscript{2} phase [12]. This spin susceptibility in the insulating phase comes from localized electrons on V site forming the B sublattice. For cation-cation distances of 2.93 Å [11], Mott Hubbard electronic correlations give rise to the above mentioned V$^{4+}$ localization. Such V$^{4+}$ centers have been observed by E. P. R. [17, 18].

In the M\textsubscript{2} structure, each chain of localized V$^{4+}$ ions is surrounded by four chains of essentially non magnetic bonded V atoms. So the magnetic character of the M\textsubscript{2} phase consists mainly of 1 dimensional chains of localized spins with only weak interactions between the chains. An antiferromagnetic intrachain exchange constant $2J \approx 700$ K has been determined from $\delta\chi$ values obtained in different alloys of Cr [12, 17], Al [22, 46], Fe [15], and in VO\textsubscript{2} under uniaxial stress [18].

At the M\textsubscript{2}-T phase transition the Heisenberg chains of spin 1/2 on the B sublattice dimerize leading to a so called spin Peierls transition (the magnetic analogue of the well known Peierls transition undergone by the one dimensional conductors). In such a dimerization, which can be viewed as opening a gap in the spin density wave spectrum, the spin susceptibility $\delta\chi$ and the spin component of the B sublattice $^{51}$V N. M. R. shift decrease [12]. The exchange constant $2J$ splits in two parts $J_1$ and $J_2$. The intradimer constant $J_1$ increases [12] while the interdimer constant $J_2$ decreases as long as the system is dimerizing in the T phase. Finally $J_2$ becomes so small that the dimers becomes magnetically isolated with a singlet triplet splitting equal to $2J_1$. When the M\textsubscript{1} phase is reached, the dimerization stopping, the spin contribution to the magnetism is not observed implying to $2J_1(M) > 2000$ K [12]. An approach to the M\textsubscript{1} limit can be obtained using uniaxial stressed VO\textsubscript{2} ($S_{z}(110)_a$) [18]. Starting from the M\textsubscript{1} phase, the effects of the stress are to contract the pairs of the sublattice A and to increase the V-V distances of site B. The equivalence between the phase diagrams of pure VO\textsubscript{2} under uniaxial stress and V$\textsubscript{1-x}$Cr$\textsubscript{x}$O$\textsubscript{2}$ alloys, and the values of the E. F. G. measured on site A in the T phase [18], show that a uniaxial stress of $\approx 1000$ bars gives a value of $2J_1 \approx 1400$ K for site B, at 300 K [12]. This estimate is confirmed by the observation of the $^{51}$V N. M. R. linewidth at 300 K under modest uniaxial stresses (Fig. 5). The $^{51}$V N. M. R. linewidth for site A is stress independent and equal to the dipolar contribution $\Delta H = 10$ G. For site B an excess
51V N. M. R. linewidth, increasing with stress, is observed and is attributed to a $J_1$ contribution, due to the mutual spin flip produced by the above $J_1$ exchange interaction. Such an effect being obtained for modest uniaxial stresses, the $M_1$ value of $J_1$ has to be quite close to the lower limit estimated above, showing that the d electrons are relatively localized on V sites in the V-V pairs of the $M_1$ phase.

The above section gives the following description of the ground state (see also [12, 47]): the $M_1$ phase is composed of relatively well separated V-V pairs in which the d electrons (mainly $d_{x^2-y^2}$ or $d_y$ orbitals) are relatively well correlated in a singlet state, while a triplet state lies a few tenth of eV above. A comparison (see Fig. 11 in ref. [12]) of this splitting with polar excitation of $d_{z^2}$ orbitals for the dimer $> 0.9$ eV (conductivity gap in the intrinsic region [38]) shows that the intradimer Coulomb interaction $U$ is larger than the intradimer transfer integral $t$. The electron-electron interactions, whose importance has been shown for the ground state, cannot be neglected for the interpretation of the experiments involving the excited states: the polar states of the ground state and to the two others $t_{2g}$ states split by the crystalline field. Such a description has been done by Zylbersztejn and Mott [38] for the transport properties of semiconducting VO$_2$ ($M_1$ phase). The influence of these effects on the transport properties of $M_1$, $T$ and $M_2$ phases of V$_{1-x}$Cr$_x$O$_2$ and V$_{1-x}$Al$_x$O$_2$ alloys has also been discussed by Villeneuve et al. [48]. A study of the optical absorption in semiconducting VO$_2$ is presented during this conference by Meranda et al. [49] and compared to a one electron V$_2$O$_{10}$ cluster calculation done by Sommers et al. [50].

4. Conclusion and the aspects of the metal insulator phase transition in VO$_2$.— The above results have shown the importance of electron correlation in all the phases of VO$_2$:

— The $M_1$ insulating phase is described in term of V-V pairs in which the cationic electrons are relatively well correlated, confirming the tendency of single electron to be paired.

— In the $M_2$ phase, half of the d electrons are localized by electron-electron correlations on zig zag vanadium sites forming linear Heisenberg chains of spin $\frac{1}{2}$.

— The $T$ phase is a transitional phase between $M_2$ and $M_1$, in which the above mentioned Heisenberg chains dimerizes.

— The metallic phase $R$ looks like the metallic phase of V$_2$O$_3$ (which exhibits with increasing temperature a metal insulator phase transition interpreted as a Mott transition [9]). In the rutile phase of VO$_2$ a somewhat similar localization effect arises when the lattice parameters increase by adding Nb impurities, with the difference that the Nb impurity adds disorder effects to the correlations effects.

We have given a description of the electronic properties of VO$_2$. However the metal insulator phase transition of VO$_2$ occurs with a quite strong structural distortion of the lattice. What are the experimental evidences of the phonons effects in this transition?

— (111)$_t$ plane of low frequency phonon has been observed in the rutile phase by X-Ray diffuse scattering [33].

— Large X-Ray Debye factors, suggesting some anomalous low frequency modes were found in the metallic phase, in contrast to the insulating $M_1$ phase [10, 11]. But it is worth noting that Debye temperatures deduced from specific heat measurements [51] don’t present such a change.

— Damped Raman lines have been observed in the rutile phase [52] which might be indicative of a large electron-phonon coupling.

— An abnormally large thermal dilatation of the $c_R$ axis [10], [53] (changing the occupancy of the different $t_{\frac{1}{2}}$ and $\pi^*$ orbitals in the metallic state, and causing the strong temperature dependance of the electric field gradient on V site [21], [54]) couples also electron and lattice effects in the metallic phase.

An attempt to understand the latent heat at the $M_1$-$R$ phase transition can be made by examining the decomposition of the transition into $R$-$M_2$ and $M_2$-$M_1$ transitions. The latent heat at the $R$-$M_2$ phase transition is very high 800 cal/mole V [12, 16] compared to 1 000 cal/mole V for the $M_1$-$R$ transition [12, 16, 51]. Only 200 cal/mole V can be attributed to the $M_2$-$M_1$ transition where only half of the lattice is distorted [18]. In this value half of the latent heat is due to the spin contribution [12]. But the origin of the entropy stabilizing the rutile metallic phase (R) remains unsolved in the absence of a self consistent model taking into account the electron-electron interactions, the phonons and the electron-phonon coupling.

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**APPENDIX**

Complementary informations on the magnetism can be obtained by the Knight shift tensor measurements. In the metallic rutile phase, the V site has an orthorombic symmetry leading to three different diagonal components whose temperature variations are presented in figure 5. All the components are negative, as expected for a strong spin contribution, and their modulus decreases with increasing temperature like the magnetic susceptibility [23]. Except for $K_y$ (the diagonal axis are indicated in figure 1), the
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This properly decomposition justify the results obtained in ref. [28] and [57] where it was assumed that the maximum in the absorption of the resonance line determines the isotropic shift. From the slope of the experimental plot, figure 7 gives a d hyperfine field \( H_d^{hf} = -80 \text{ kOe/}\mu_B \) in good agreement with those obtained by \( \text{V}^{4+} \) E. P. R. measurements in rutile structure [56]. The orbital susceptibility \( \chi_o = 0.6 \times 10^{-4} \text{ emu/mole V} \) is found to be one order of magnitude lower than that of the spin susceptibility \( \chi_d = 6.2 \times 10^{-4} \text{ emu/mole V} \) \((T = 370 \text{ K})\).

For the \( V_{1-x}\text{Nb}_x\text{O}_2 \) alloys the magnetic susceptibility increases rapidly with increasing \( x \) [28]. The increase in the susceptibility is much bigger than the Van Vleck contribution estimated above for VO₂. This increase must therefore be attributed to an increase in the d spin susceptibility. The \( ^{51}\text{V} \) Knight shift, \( K \), measured for different compositions \( x \), is shown in figure 8 in a \( K \) versus \( \chi \) (total susceptibility) diagram.

Within the experimental errors all the points fit the same straight line as done in reference [17]. Knight shift accounting for the bulk V sites, the increase of its negative part, when \( x \) increases, corresponds to an increase of the d susceptibility which is not localized around the impurity. More precisely if the impurity potential is repulsive enough leading to \( \text{Nb}^{4+} \rightarrow \text{Nb}^{5+} \)
formation and if we assume that the extra electron is shared by all the V atom, the experimental points for \( x = 0.05 \) (\( \cdot \)) must be on the dotted line drawn in figure 8. We see that the agreement is quite bad. If the electron is spread over the nearest neighbours, one must observe near the central line, quite important satellites lines of measurable shift or strong deviation of the Knight shift value from the above straight line for the higher Nb concentrations (\( x > 0.1 \)). All the above effects are not observed [21]. The alignment shown in figure 8 means that the increase in the \( \Delta x \) susceptibility, in the metallic phase, with Nb concentration, is quite homogenous, that is to say with no important local effects around the impurity. For the higher concentrated alloys studied, experimental errors reported in figure 8 are quite big, because of the broad linewidth of the \( ^{51}\text{V} \) resonance line. It should be noticed that, in these compounds the linewidth \( \Delta H \), increases strongly with the applied magnetic field \( H \) (\( \Delta H/H \approx 5.6 \times 10^{-5}, 7.3 \times 10^{-3} \) and \( 9.5 \times 10^{-3} \) for \( x = 0.10, 0.12 \) and 0.135 respectively [21]).

References

[31] Nygren, M., Chemical Communications (University of Stockholm) II (1975).
[39] According to Goodenough [4] the \( l \) band comes from direct cation-cation overlap along the \( c_{\parallel} \) axis (\( d_{2g} \) and \( d_{3g} \) orbitals; the directions \( x, y, z \) are defined in figure 1) whereas the others two \( t_{2g} \) orbitals (\( d_{xy} \) and \( d_{yz} \) mix with the anion \( 2p \) orbitals forming a wider \( n^* \) band.
[40] Similar size effects have been observed in the \( V_{1-x}W_{2}O_{5} \) alloys (M. Israelsson and L. Kihlborg, Mater. Res. Bull. 5 (1970) 19), leading to an increase of correlation effects which might explain the large linear term found in the temperature dependance of the specific heat of the metallic alloys corresponding to \( x = 0.14 \). \( \gamma = (80 + 5) \times 10^{-6} \) cal K\(^{-2}\)/mole V [36].
[43] A best fit plot of the magnetic susceptibility for the \( Vo_{3}Nba_{2}O_{5} \) compound gives:
\[
\chi = 3 \times 10^{-5} + 0.5(T + 5) \text{emu/mole}
\]
The orbital component (\( 3 \times 10^{-5} \) emu/mole) is equal to that deduced in metallic \( Vo_{5} \) (Fig. 7) and the Curie constant corresponds exactly to the ionic formula \( V_{0.3}Na_{0.7}\)O\(_{5}\). Subtracting this orbital component from the total magnetic susceptibility reported in figure 4, will decrease only by a few percent the Curie constant value shown in figure 4b, without changing the interpretation given in the text.
Except for the $K_z$ component, the $^{51}$V chemical shift tensors corresponding to the paired sites in $M_1$ and $M_2$ phases are the same [12]. The difference in the $z$ component chemical shift might be due to the different tilting of the pairs along the $z$ direction in the above phases.


