



HAL
open science

METAL-INSULATOR PHASE TRANSITION IN VO₂

Jean Pouget, H. Launois

► **To cite this version:**

Jean Pouget, H. Launois. METAL-INSULATOR PHASE TRANSITION IN VO₂. Journal de Physique Colloques, 1976, 37 (C4), pp.C4-49-C4-57. 10.1051/jphyscol:1976408 . jpa-00216522

HAL Id: jpa-00216522

<https://hal.science/jpa-00216522>

Submitted on 4 Feb 2008

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

METAL-INSULATOR PHASE TRANSITION IN VO₂

J. P. POUGET and H. LAUNOIS

Laboratoire de Physique des Solides (*)
 Université Paris-Sud, 91405 Orsay, France

Résumé. — On passe en revue les effets d'alliages et de comportement sous contrainte uniaxiale des propriétés structurales 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 V_{1-x}Nb_xO₂, (ii) dans les phases isolantes de VO₂ pur à pression ambiante (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 V_{1-x}Nb_xO₂ 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 ($\Delta S = 1.5 \text{ k/VO}_2 \text{ unit}$) 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 V₂O₃, 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 V_{1-x}Nb_xO₂ system. The properties of the insulating phases, of VO₂ under uniaxial stress and of the V_{1-x}Cr_xO₂ 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)_R and (1 $\bar{1}$ 0)_R directions for the A and B vanadium atoms, respectively. The

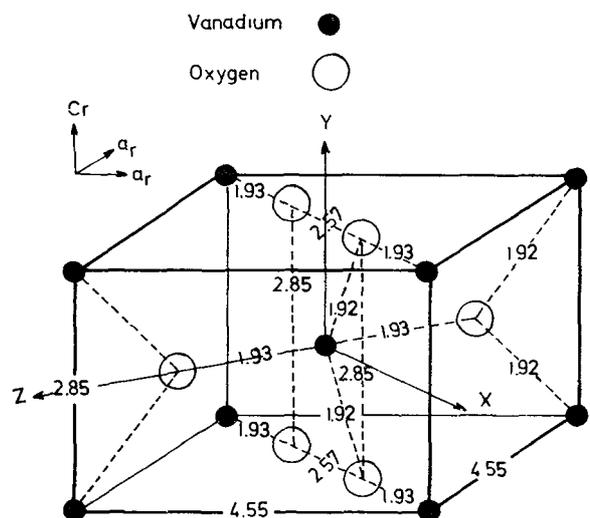


FIG. 1. — Rutile cell of the high-temperature phase of VO₂. Distances, in angstrom, are taken from reference [10].

(*) Associé au Centre National de la Recherche Scientifique.

monoclinic insulating phase (M_1) can be presented as the result of a two components distortion : a pairing of V atoms along the $(001)_R$ 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 $(001)_R$ axis, as schematically shown in figure 2a.

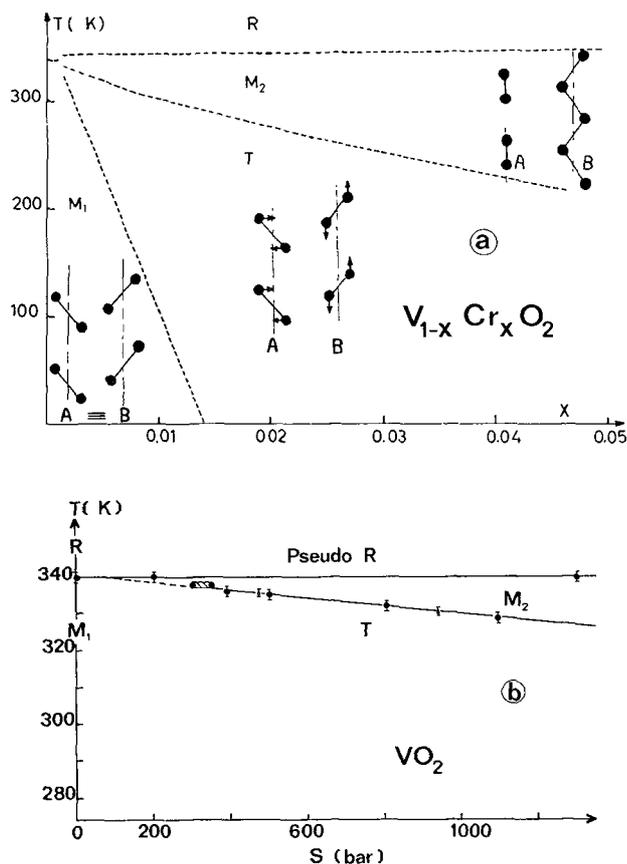


FIG. 2. — a) The phase diagram of $V_{1-x}Cr_xO_2$ alloys (after ref. [13]). In each insulating phase, vanadium chains of the A and B sublattices, contained in the $(1\bar{1}0)_R$ and $(110)_R$ planes respectively, are represented. The arrows in the T phase indicate the displacement of the V atoms when 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 thousandths 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 $(001)_R$ 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 $(001)_R$ 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 Goode-nough 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 $(110)_R$ 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 .

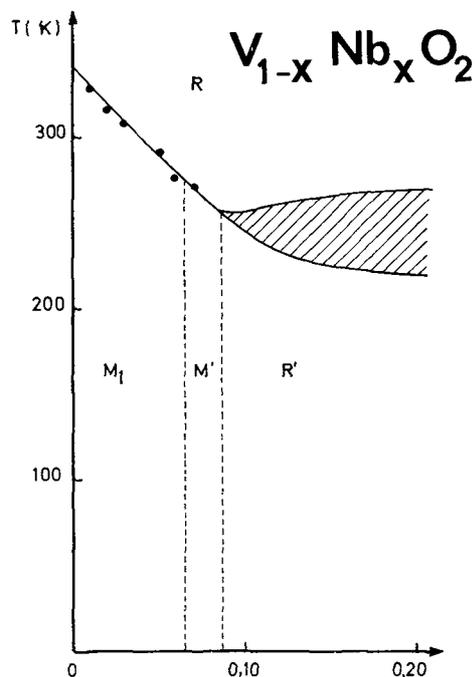


FIG. 3. — The phase diagram of $V_{1-x}Nb_xO_2$ alloys deduced from X ray measurements. After reference [20].

Reyes *et al.* [19] have recently claimed that the T phase might be a mixed phase region between M₁ and M₂. 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 Cr³⁺ and V⁴⁺ centers [17]) demonstrate that there is a big difference in the symmetry of M₁ and M₂ 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-M₂ and M₂-R phase transitions [12, 16, 22]. In some of the samples a broadening of the M₁-T transition (where no measurable latent heat had been reported [12, 16]) was observed. Because of the large variation of the M₁-T transition temperature with impurity concentration, sample inhomogeneities might yield to a such broadening. In addition, such mixing effects couldn't arise in VO₂ under uniaxial stress.

Figure 3 presents the phase diagram, determined by Villeneuve *et al.* [20, 23] for the V_{1-x}Nb_xO₂ system. At low impurity concentration, the insulating phase M₁ 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 V⁴⁺ state to the V³⁺ state in the insulating phase M₁. In this phase the impurities break the pairs and create one V³⁺ ion in the Nb case [28] or two V³⁺ ions in the W case [29], giving rise to Curie Weiss contribution to the magnetic susceptibility. Such V³⁺ 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 $12^\circ \pm 1^\circ$ percent of V³⁺ ions. Such a decrease, proportional to the number of V³⁺ created, suggests that the pair breaking is the main mechanism to destabilize the insulating phase [32]. Such a V³⁺ state, appearing with so different impurities (as well as the V⁵⁺ state found with Cr [12], Al, Fe impurities) is difficult to understand in the framework of a pure band model for the M₁ phase. On the other hand, the V³⁺ or V⁵⁺ state formation is explained easily by electronic transfer in a singlet bond *molecular* picture of the insulating phase of VO₂ [9], [32].

Figure 3 shows that the structure of the low temperature region, obtained by usual X ray methods, change from monoclinic M₁ 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)_R and (1 $\bar{1}$ 0)_R 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 M₁ 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. — VO₂ in its metallic phase is a poor metal with resistivity of the order of 10^{-4} (Ω cm)⁻¹ [6] which is comparable to that of V₂O₃ [9]. The spin susceptibility deduced from the plot of the ⁵¹V 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 χ_d is only 25 % lower than the spin susceptibility of V₂O₃ : $\chi_d \sim 8 \times 10^{-4}$ emu/mole V at 155 K [35]. The above comparison suggests a similar description for the metallic phases of the two compounds. In the VO₂ case, one can deduce, from the spin susceptibility, an effective density of states at the Fermi level : $n^*(E_F) = 10$ states/eV and spin direction. This enhanced value is in favor of quite important electron-electron interactions in the metallic phase of VO₂. 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, Zylbersztein and Mott [38] view the metallic VO₂ as similar to transition metals like Pt or Pd : electrons in a comparatively wide band (π^*) screening out the interaction between the electrons in a narrow overlapping band (t_{\parallel}) [39]. It is difficult from the study of pure VO₂ to differentiate clearly between the above models. Much more can be learnt from the study of the V_{1-x}Nb_xO₂ system in its high temperature rutile phase.

Introducing a Nb atom (isoelectronic of V atom) in VO₂ leads to the following local effects (32) :

- local repulsive one electron potential : $E_4 d > E_3 d$,
- local attractive electron-electron interaction term : $U_4 d < U_3 d$,
- 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 Nb^{4+} in the metallic state is quite unusual (by comparison with the Cr impurities in metallic VO_2 which looks like 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 π^* bandwidths and the increase of the c/a ratio will destabilize $t_{||}$ with respect to π^* . 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 ($T > 400$ K), for $x \sim 0.12-0.15$, 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 decrea-

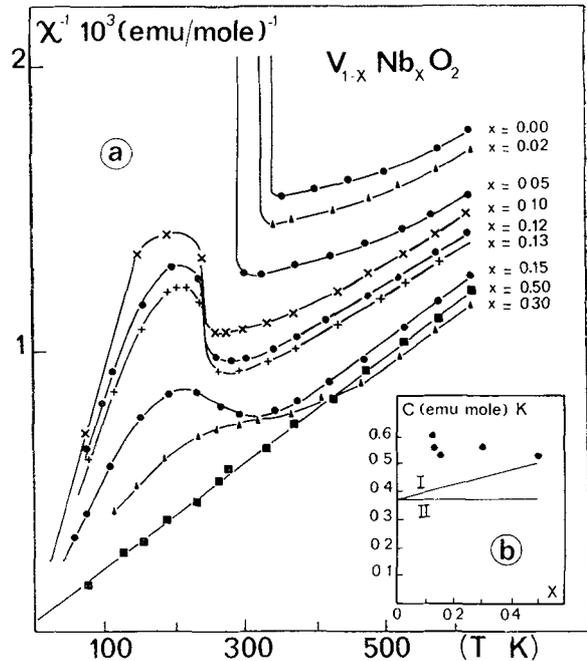
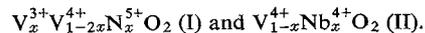


FIG. 4. — a) Inverse susceptibility χ^{-1} of the concentrated alloys $V_{1-x}Nb_xO_2$ vs temperature (after ref. [20] and [28]). b) High temperature Curie constants obtained from (a) vs Nb concentration. Solid lines correspond to chemical formulas



ses with increasing x and for $x \sim 0.20$ [42] 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) $V_x^{3+}V_{1-2x}^{4+}Nb_x^{5+}O_2$ and (II) $V_{1-x}^{4+}Nb_x^{4+}O_2$. 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 $x \simeq 0.33$ [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 $V_x^{3+}V_{1-2x}^{4+}Nb_x^{5+}O_2$. 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^{4+}) 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

Nb⁵⁺ site, leading to the insulating state. However the free movement of the V³⁺ in around the Nb center (which gained kinetic energy) will be strongly obstructed by the increasing number of Nb⁵⁺ trap and the decreasing number of V⁴⁺ ions. In the insulating state, because of the spin polaron effect, the Curie constant is still larger than the calculated value from the V_x³⁺V_{1-2x}⁴⁺Nb_x⁵⁺O₂ configuration as shown in figure 4b, but the difference between the experimental and calculated value decreases with the decreasing number of V⁴⁺ ions. It can also be expected lattice polaronic effects, arising from the fact that around V³⁺ ion the V-O distances are larger than those around V⁴⁺ ions. In such a case lattice relaxation favors a trapping state for the V³⁺ ions.

There is strong evidence of the similar behaviour in the VO_{2-x}F_x alloys, as indicated by :

- 1) strong expansion of the lattice with x [27] ;
- 2) Curie Weiss like susceptibility exhibiting quite big Curie constant $C \sim 0.8$ emu/mole for $x \sim 0.3$ [27] ;
- 3) a metal-insulator transition with x : VOF being, as V_{0.5}Nb_{0.5}O₂, a paramagnetic insulator with similar weak A. F. interaction temperature : $\theta \sim 10$ K [44].

3. The low temperature insulating phases. — The crystallographic relations among the M₁, T, M₂ insulating phases, presented in the first part are shown schematically in figure 2a. We have also shown that the magnetic properties of the M₁ 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 M₂ phase and, through the T phase, add the remaining cationic distortion to obtain finally the M₁ phase.

The M₂ 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 M₁ 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 ($\delta\chi \sim 2 \times 10^{-4}$ emu/mole V) giving rise to the increase in the magnetic susceptibility observed in the M₂ 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 V⁴⁺ localization. Such V⁴⁺ centers have been observed by E. P. R. [17, 18].

In the M₂ structure, each chain of localized V⁴⁺ ions is surrounded by four chains of essentially non magnetic bonded V atoms. So the magnetic character of the M₂ phase consists mainly of 1 dimensional chains of localized spins with only weak interactions between the chains. An antiferromagnetic intrachain

exchange constant $2J \sim 700$ K has been determined from $\delta\chi$ values obtained in different alloys of Cr [12, 17], Al [22, 46], Fe [15], and in VO₂ under uniaxial stress [18].

At the M₂-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 ⁵¹V 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 M₁ phase is reached, the dimerization stopping, the spin contribution to the magnetism is not observed implying to $2J_1(M_1) > 2000$ K [12]. An approach to the M₁ limit can be obtained using uniaxial stressed VO₂ ($S_{\parallel}(110)_R$) [18]. Starting from the M₁ 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 VO₂ under uniaxial stress and V_{1-x}Cr_xO₂ alloys, and the values of the E. F. G. measured on site A in the T phase [18], show that a uniaxial stress of ~ 1500 bars gives a value of $2J_1 \sim 1400$ K for site B, at 300 K [12]. This estimate is confirmed by the observation of the ⁵¹V N. M. R. linewidth at 300 K under modest uniaxial stresses (Fig. 5). The ⁵¹V N. M. R. linewidth for site A is stress independant and equal to the dipolar contribution $\Delta H = 10$ G. For site B an excess

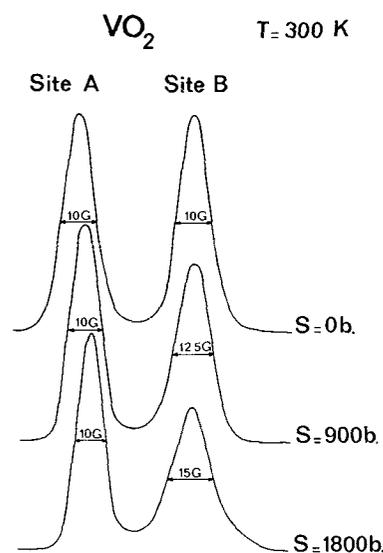


FIG. 5. — Stress variation of the linewidth of the ($+\frac{1}{2} \rightarrow -\frac{1}{2}$) ⁵¹V nuclear transition for A and B sites of VO₂ at room temperature (the applied magnetic field H is along the $(1\bar{1}0)_R$ direction, see ref. [18]).

^{51}V N. M. R. linewidth, increasing with stress, is observed and is attributed to a T_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 $d_{||}$ orbitals) are relatively well correlated in a singlet state, while a triplet state lies a few tenths of eV above. A comparison (see Fig. 11 in ref. [12]) of this splitting with polar excitation of $d_{||}$ orbitals for the dimer > 0.9 eV (conductivity gap in the intrinsic region [38]) shows that the intraatomic 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 Zylbersztein 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 $\text{V}_{1-x}\text{Cr}_x\text{O}_2$ and $\text{V}_{1-x}\text{Al}_x\text{O}_2$ 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_2O_{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 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_2O_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? :

— $(111)_R$ 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 $t_{||}$ and π^* 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.

Many of the above results arise from the collaboration between several groups and particularly with G. Villeneuve, T. M. Rice and P. Meranda. We want also to thank A. Casalot, R. Comes, J. P. D'Haenens, J. Friedel, D. Kaplan, P. Lederer, M. Nygren, C. B. Sommers and A. Zylberstein for stimulating discussions and early disclosure of their results.

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 orthorhombic 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

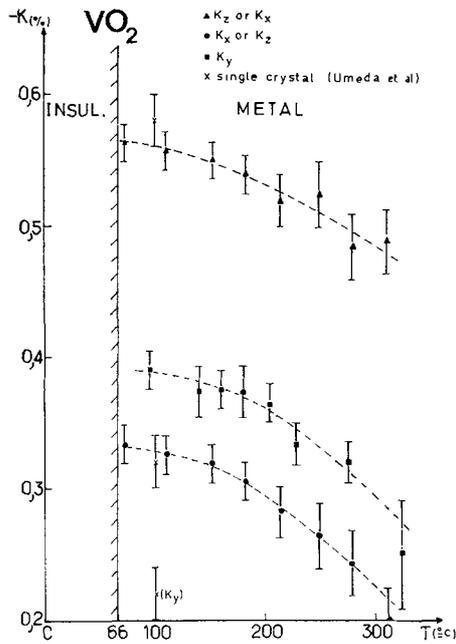


FIG. 6. — Temperature dependence of the three diagonal components of the ⁵¹V Knight shift tensor in the metallic phase of VO₂.

two others components are in agreement with Umeda *et al.* [55] measurements ; a much better agreement is obtained for the E. F. G. measurements [21, 54]. The isotropic part of the Knight shift tensor K allows to obtain the decomposition of the magnetic susceptibility (measured on powder) in a plot K versus χ (Fig. 7).

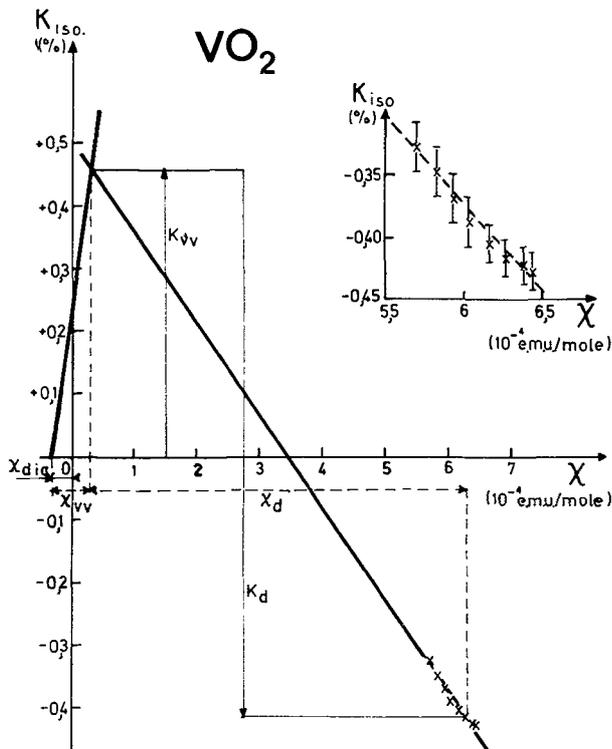


FIG. 7. — ⁵¹V isotropic Knight shift vs macroscopic susceptibility in the metallic phase of pure VO₂. Diamagnetic, orbital and spin contributions are separated here.

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 V⁴⁺ E. P. R. measurements in rutile structure [56]. The orbital susceptibility $\chi_{vv} = 0.6 \times 10^{-4} \text{ emu/mole V}$ 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}Nb_xO₂ 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 ⁵¹V Knight shift, K , measured for different compositions x , is shown in figure 8 in a K versus χ (total susceptibility) diagram.

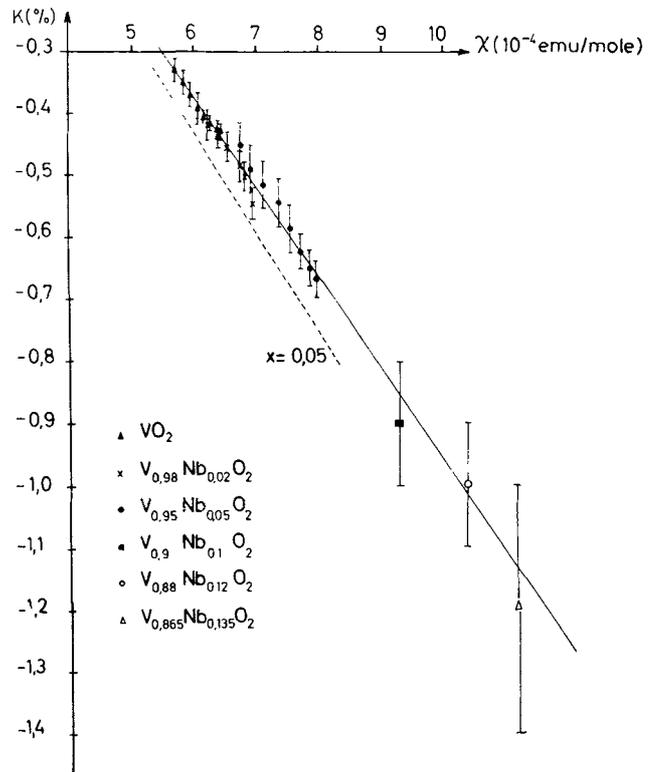


FIG. 8. — ⁵¹V Knight shift of V_{1-x}Nb_xO₂ alloys vs macroscopic susceptibility in the rutile phase. The solid line is drawn through the experimental points corresponding to pure VO₂. The dotted line, drawn for $x = 0.05$, assumes a complete electron transfer from Nb atoms to V atoms.

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 Nb⁴⁺ → Nb⁵⁺

formation and if we assume that the extra electron is shared by all the V atom, the experimental points for $x = 0.05$ (·) 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 d

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}V resonance line. It should be noticed that, in these compounds the linewidth ΔH , increases strongly with the applied magnetic field H ($\Delta H/H \sim 5.6 \times 10^{-3}$, 7.3×10^{-3} and 9.5×10^{-3} for $x = 0.10$, 0.12 and 0.135 respectively [21]).

References

- [1] MORIN, F. J., *Phys. Rev. Lett.* **3** (1959) 34.
- [2] UMEDA, J., KUSUMOTO, H., NARITA, K. and YAMADA, E., *J. Chem. Phys.* **42** (1965) 1458 ;
KOSUGE, K., *J. Phys. Soc. Japan* **22** (1967) 551.
- [3] ADLER, D., BROOKS, H., FEINLEIB, J. and PAUL, W., *Phys. Rev.* **155** (1967) 851.
- [4] GOODENOUGH, J. B., *Progress in Solid State Chemistry*, edited by H. Reiss (Pergamon, Oxford) 1971, Vol. 5, p. 351.
GOODENOUGH, J. B., *J. Solid State Chem.* **3** (1971) 490.
- [5] BERGLUND, C. N. and GUGGENHEIM, H. J., *Phys. Rev.* **185** (1969) 1022.
- [6] PAUL, W., *Mater. Res. Bull.* **5** (1970) 691.
- [7] HEARN, C. J., *J. Phys. C* **5** (1972) 1317.
- [8] GOODENOUGH, J. B., *Phys. Rev.* **117** (1960) 1442.
- [9] RICE, T. M., MCWHAN, D. B. and BRINKMAN, W. F., Proc. 10th Int. Conf. on Semiconductors (U. S. A. E. C. 1970) p. 293.
- [10] MCWHAN, D. B., MAREZIO, M., REMEIKA, J. P. and DERNIER, P. D., *Phys. Rev.* **B 10** (1974) 490.
- [11] MAREZIO, M., MCWHAN, D. B., REMEIKA, J. P. and DERNIER, P. D., *Phys. Rev.* **B 5** (1972) 2541.
- [12] POUGET, J. P., LAUNOIS, H., RICE, T. M., DERNIER, P., GOSSARD, A., VILLENEUVE, G. and HAGENMULLER, P., *Phys. Rev.* **B 10** (1974) 1801.
- [13] VILLENEUVE, G., DRILLON, M. and HAGENMULLER, P., *Mater. Res. Bull.* **8** (1973) 1111.
- [14] DRILLON, M. and VILLENEUVE, G., *Mater. Res. Bull.* **9** (1974) 1199.
- [15] POLLERT, E., VILLENEUVE, G., MENIL, F. and HAGENMULLER, P., *Mater. Res. Bull.* **11** (1976) 159.
- [16] KOSUGE, K. and KACHI, S., *Mater. Res. Bull.* **11** (1976) 255.
- [17] D'HAENENS, J. P., KAPLAN, D. and MERENDA, P., *J. Phys. C Solid state Phys.* **8** (1975) 2267.
- [18] POUGET, J. P., LAUNOIS, H., D'HAENENS, J. P., MERENDA, P. and RICE, T. M., *Phys. Rev. Lett.* **35** (1975) 873.
- [19] REYES, J. M., SEGEL, S. L. and SAYER, M., *Can. J. Phys.* **54** (1976) 1.
- [20] VILLENEUVE, G., thesis, Bordeaux (1974) (unpublished).
- [21] POUGET, J. P., thesis, Orsay (1974) (Unpublished).
- [22] DRILLON, M., 3rd cycle thesis Bordeaux (1974) (Unpublished).
- [23] VILLENEUVE, G., BORDET, A., CASALOT, A., POUGET, J. P., LAUNOIS, H. and LEDERER, P., *J. Phys. Chem. Solids* **33** (1972) 1953.
- [24] HORLIN, T., NIKLEWSKI, T. and NYGREN, M., *Mater. Res. Bull.* **8** (1973) 179.
- [25] NYGREN, M. and ISRAELSSON, M., *Mater. Res. Bull.* **4** (1969) 881.
- [26] VILLENEUVE, G., private Communication.
- [27] BAYARD, M., POUCHARD, M., HAGENMULLER, P. and WOLD, A., *J. Solid State Chem.* **12** (1975) 41.
- [28] POUGET, J. P., LEDERER, P., SCHREIBER, D. S., DAUNOIS, H., WOHLLEBEN, D., CASALOT, A. and VILLENEUVE, G., *J. Phys. Chem. Solids* **33** (1972) 1961.
- [29] HORLIN, T., NIKLEWSKI, T. and NYGREN, M., *Mater. Res. Bull.* **7** (1974) 1515.
- [30] D'HAENENS, J. P., KAPLAN, D., MERENDA, P. and TUCHENDLER, J., Proceedings of the 12th International Conference on the Physics of Semiconductors, Stuttgart (1974).
- [31] NYGREN, M., *Chemical Communications* (University of Stockholm) **11** (1973).
- [32] LEDERER, P., LAUNOIS, H., POUGET, J. P., CASALOT, A. and VILLENEUVE, G., *J. Phys. Chem. Solids* **33** (1972) 1969.
- [33] COMES, R., FELIX, P., LAMBERT, M. and VILLENEUVE, G., *Acta Crystallogr. A* **30** (1974) 55.
- [34] RICE, T. M., Proc. A. I. P. Conference on Magnetism and Magnetic Materials p. 1406, Denver (1972).
- [35] JONES, E. D., *Phys. Rev.* **137** (1965) A 978 ;
GOSSARD, A. C., MENTH, A., WARREN, W. W. Jr and REMEIKA, J. P., *Phys. Rev.* **B 3** (1971) 3993.
- [36] MCWHAN, D. B., REMEIKA, J. P., MAITA, J. P., OKINAKA, H., KOSUGE, K. and KACHI, S., *Phys. Rev.* **B 7** (1973) 326.
- [37] BRINKMAN, W. F. and RICE, T. M., *Phys. Rev.* **B 2** (1970) 4302.
- [38] ZYLBERSZTEJN, A. and MOTT, N. F., *Phys. Rev.* **B 11** (1975) 4383.
- [39] According to Goodenough [4] the t_{\parallel} band comes from direct cation-cation overlap along the c_R axis ($d_{x^2-y^2}$ orbitals ; the directions x, y, z are defined in figure 1) whereas the others two t_{2g} orbitals (d_{xz} and d_{yz}) mix with the anion $2p$ orbitals forming a wider π^* band.
- [40] Similar size effects have been observed in the $V_{1-x}W_xO_2$ alloys (M. Israelsson and L. Kihlberg, *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 $x = 0.14 : \gamma = (80 + 5) 10^{-4}$ cal K^2 /mole V [36].
- [41] MOTT, N. F., *Metal-Insulator Transitions* (Taylor and Francis, London) 1974.
- [42] VILLENEUVE, G., LAUNAY, J. C. and HAGENMULLER P., *Solid State Commun.* **15** (1975) 1683.
- [43] A best fit plot of the magnetic susceptibility for the $V_{0.5}Nb_{0.5}O_2$ compound gives :
 $\chi = 3 \times 10^{-5} + 0.5/(T + 5)$ emu/mole.
The orbital component (3×10^{-5} emu/mole) is equal to that deduced in metallic VO_2 (Fig. 7) and the Curie constant corresponds exactly to the ionic formula $V_{0.5}^{3+}Nb_{0.5}^{5+}O_2$. Subtracting this orbital component from the total magnetic susceptibility reported in figure 4a, will decrease only by a few percent the Curie constant value C shown in figure 4b, without changing the interpretation given in the text.
- [44] CHAMBERLAND, B. L., SLEIGHT, A. W. and CLOUD, W. H., *J. Solid State Chem.* **2** (1970) 49.

- [45] Except for the K_z component, the ⁵¹V chemical shift tensors corresponding to the paired sites in M₁ and M₂ 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.
- [46] VILLENEUVE, G., DRILLON, M., HAGENMULLER, P., NYGREN, M., POUGET, J. P., CARMONA, F. and DELHAES, P. (to be published).
- [47] MOTT, N. F. and FRIEDMAN, L., *Phil. Mag.* **30** (1974) 389.
- [48] VILLENEUVE, G., DRILLON, M., LAUNAY, J. C., MARQUESTAUT, E. and HAGENMULLER, P., *Solid State Commun.* **17** (1975) 657.
- [49] MERANDA, P., KAPLAN, D. and SOMMERS, C., *J. Physique Colloq.* **37** (1976) C4-59.
- [50] SOMMERS, C., DE GROOT, R., KAPLAN, D. and ZYLBERSZTEJN, A., *J. Physique Lett.* **36** (1975) L-157.
- [51] CHANDRASHEKHAR, G. V., BARROS, H. L. C. and HONIG, J. M., *Mater. Res. Bull.* **8** (1973) 369.
- [52] SRIVASTAVA, R. and CHASE, L. L., *Phys. Rev. Lett.* **27** (1971) 727.
- [53] RAO, K. V. K., NAIDU, S. V. N. and IYENGAR, L., *J. Phys. Soc. Japan* **23** (1967) 1380.
- [54] UMEDA, J. I., NARITA, K. and KUSUMOTO, H., *Hitachi Rev.* **204** (1968).
- [55] UMEDA, J. I., ASHIDA, S., KUSUMOTO, H. and NARITA, K., *J. Phys. Soc. Japan* **21** (1966) 1461.
- [56] SHIMIZU, T., *J. Phys. Soc. Japan* **23** (1967) 848.
- [57] FORD, C. J., SEGEL, S. L., SEYMOUR, E. F. W., HYLAND, G. J., *Phys. kond. Mater.* **14** (1972) 111.