Charge gap and magnetism across the metal-insulator transition of the quasi-1D compounds $(Sr,Na)_x V_6O_{15}$

Y. Fagot-Revurat[1] , H.Cercellier[1], D. Malterre[1],
C. Sellier[2], E. Janod[2], F. Boucher[2], B. Corraze[2], C. Payen[2], V. Fernandez[2]
F. Bertran[3], C. Marin[4]

[1]Laboratoire de physique des matériaux, UMR 7556, université Henri Poincaré, BP 256, F-54506 Vandoeuvre-les-Nancy cedex, France.
[2]Institut des Matériaux Jean Rouxel, Université de Nantes - CNRS, F-44322 Nantes Cedex 3, France.
[3]Laboratoire pour l'utilisation du Rayonnement Electromagnétique, Université Paris-sud, F-91405 Orsay Cedex, France.
[4]DRFMC, CENG-CEA Avenue des Martyrs, F-38000 Grenoble, France.

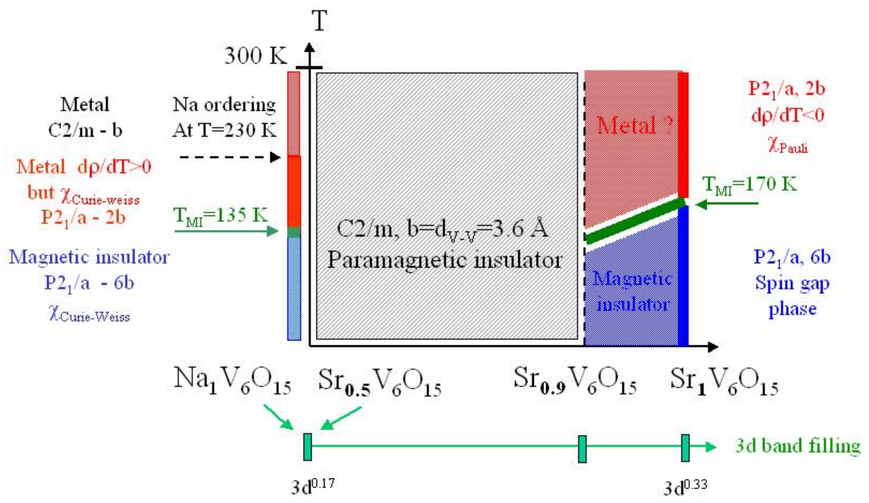
ABSTRACT :

The vanadium bronzes β-$A_xV_6O_{15}$ (A=Sr, Ca, Na, Li, Ag …), first discovered in the 80's, are mixed-valence compounds V^{4+} ($3d^1$)/V^{5+} ($3d^0$) presenting very exciting physics such as low dimensionnal electronic properties, metal-insulator transition and superconductivity. The stoechiometric samples $(Na,Sr)_{x=1}V_6O_{15}$ present a complex phase transition associating a metal-insulator transition (MIT), a structural transition and a charge ordering occuring at T_{MI}=170 K for $Sr_1V_6O_{15}$ and T_{MI}=135 K for $Na_1V_6O_{15}$. Superconducting properties have been also evidenced recently at high pressure below T=9 K in NaV_6O_{15}.

At room-temperature, they present « metallic » properties ($\rho_{//} \approx 10^{-3}$ Ω.cm and $\rho_\perp/\rho_{//} \approx 100$) with a quasi-1D Fermi surface (from band structure calculations). Surprisingly, NaV_6O_{15} has a metallic resistivity associated with a Curie-Weiss magnetic susceptibility whereas SrV_6O_{15} is semiconducting with a Pauli-like paramagnetic suceptibility suggested delocalized carriers ! The ordering of the Sr (for x>0.9) and Na (for T<230 K) atoms lead to a doubling of the lattice parameter along the b-axis. Only one type of $V^{4.83+}$ and $V^{4.66+}$ site are observed respectively for NaV_6O_{15} and SrV_6O_{15} above the MIT.

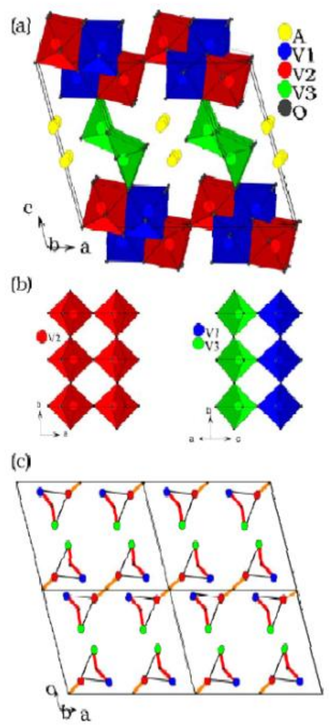
Below the Metal-insulator transition (MIT), a tripling of the lattice parameter is observed in both cases associated with a charge ordering. Nevertheless, magnetism is still present at low-T : a Curie-Weiss susceptibility is observed in the case of NaV_6O_{15} whereas a spin-gap phase is revealed in the case of SrV_6O_{15}. A charge gap of 200 meV is evidenced below the TMI in $Sr_1V_6O_{15}$ by angle-integrated photoemission measurements associated with a stabilization of the correlated d band. One of the key point to understand this complex phase transition could be the Fermi wave vector k_F which can be extracted from ARPES measurements on single crystals.

$A_xV_6O_{15}$ PHASE DIAGRAM



→ The MIT has been investigated by ARPES both as function of doping In $Sr_xV_6O_{15}$ and as function of temperature in $Sr_1V_6O_{15}$ and NaV_6O_{15}.

$Sr_xV_6O_{15}$ structure

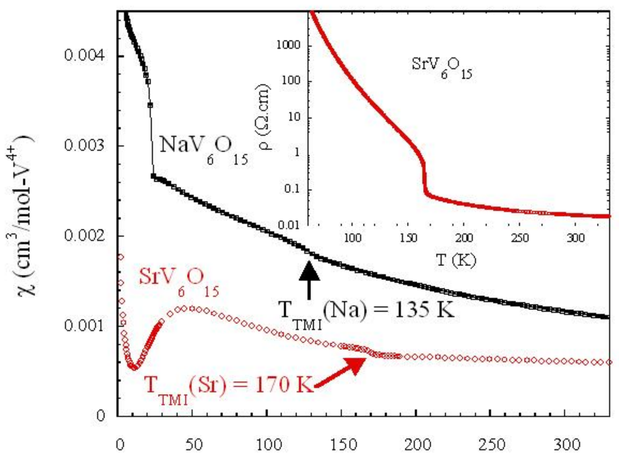


(a) C2/m space group

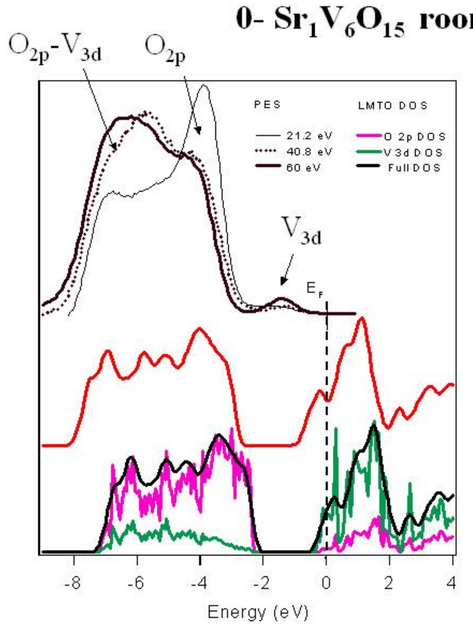
(b) Two legs ladder structure of the V_2 (left) and V_1-V_3 (right)

(c) Schematic drawing of the leading V-V transfert integrals in (a,c) plane as proposed from Extended Hückel Tight Binding calculations *[M.L. Doublet and M.B. Lepetit, Phys. Rev. B, 2005]*. The main interactions are within the nearly orthogonal V_2-V_2 and V_1-V_3 ladders.

Transport and magnetic measurements



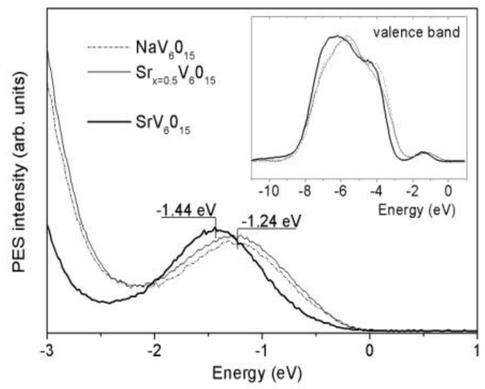
0- $Sr_1V_6O_{15}$ room-T electronic structure



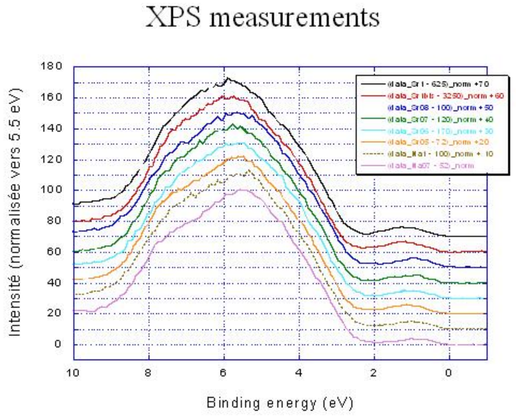
Angle-integrated photoemission spectra obtained on $Sr_1V_6O_{15}$ powder samples for different photon energies. The energy dependence allows to clearly identify O_{2p} bands for binding energies higher than 3 eV and V_{3d} spectral feature around 1.4 eV. A comparison with LMTO Band structure calculations is presented. As expected, the O_{2p} spectral feature is well described. On one hand, the O_{2p}-V_{3d} hybridization is corroborated by the strong increase of this feature with increasing the photon energy. On the other hand, the calculated V_{3d} density of occupied states is maximum at the Fermi energy whereas the experimental one shows a maximum around 1.4 eV. Even far from half filling ($3d^{0.33}$), the observation of a strong incoherent peak at a so high energy is probably due to strong correlations, this 3d band constituting the lower Hubbard band observed in numerous vanadium oxides.
In addition, no spectral weight has been measured at E_F signing *a quasi-1D metallic behavior* and/or *polaronic effects (small polarons)*.

1 – Electronic structure as function of doping

UPS measurements at 60 eV

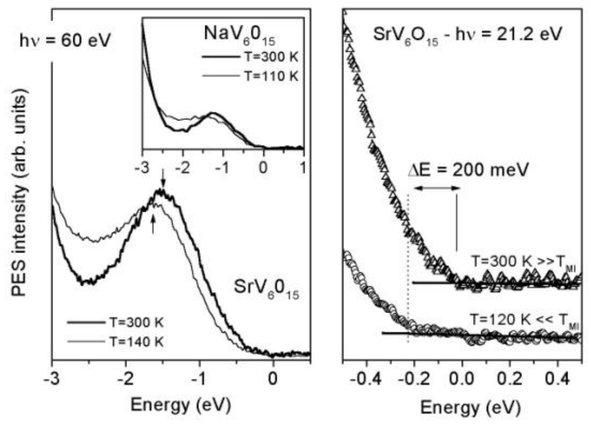


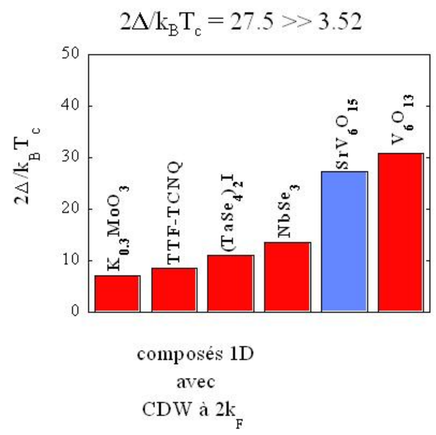
XPS measurements



The position of the V_{3d} incoherent peak (partially) follows the 3d band filling : E=1.24 eV in the case of $Sr_{0.5}V_6O_{15}$ and NaV_6O_{15} which have the same filling ($3d^{0.17}$) and E=1.44 eV for $Sr_1V_6O_{15}$ ($3d^{0.33}$). This is corroborated by XPS measurements suggesting that these measurements are bulk-like !

2 - Charge gap accross the MIT: opening of a gap Δ ≈ 200 meV

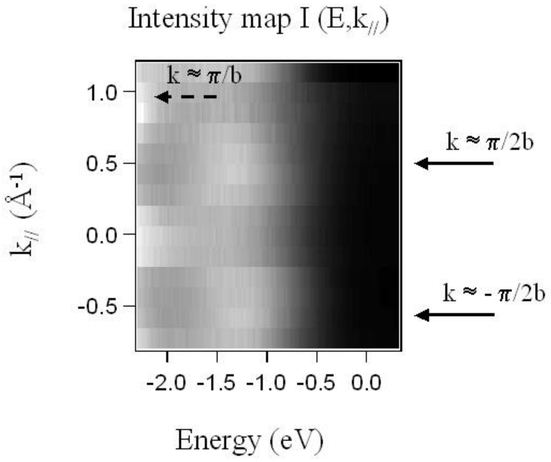




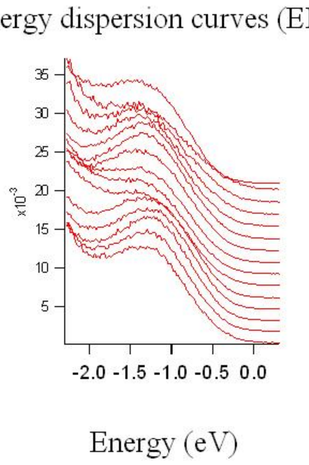
The V_{3d} spectral feature is stabilized below the metal-insulator transition (energy gain≈150 meV). In addition, a precise investigation of the spectral weight close to the Fermi level evidences the opening of gap in the occupied density of states in agreement with an increase with more than one order of magnitude of the resistivity and the insulating nature of the low-T phase. The strong BCS ratio measured in this compound is higher than those measured in standard $2k_F$ Peierls compounds. It is closer to polaronic compounds like Ti_4O_7…

3 – Angle-resolved results on $Sr_{0.5}V_6O_{15}$ single crystals

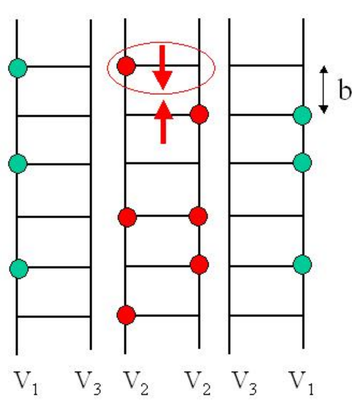
Intensity map I (E,$k_{//}$)



Energy dispersion curves (EDC)



Schematic charge distribution



→ $Sr_1V_6O_{15}$: $3d^{0.33}$ ⇔ 6 + 6 =12 e⁻/36 V

($Sr_{0.5}V_6O_{15}$ and NaV_6O_{15} : $3d^{0.17}$ ⇔ 6 e⁻/36 V)

DISCUSSION

→origin of the absence of spectral weight at E_F (non Fermi liquid, small polarons…)

→ mechanism of this (very) complex transition :

$2k_F$ Charge density wave excluded by the presence of magnetism below T_{MI}

$4k_F$ Charge density wave (in a correlated metal) ?

2b → 6b (×3) a tripling of the lattice parameter is possible if ρ=1/3=0.33 e⁻/site (CDW at $4k_F$) or ρ=2/3=0.66 e⁻/site (CDW at $2k_F$)

Others…

⇒ to answer we need the k_F value measured by ARPES

In NaV_6O_{15} : k_F=0.22 Å^{-1} ≈ π/4b in the $P2_1/a$ phase (from Okazaki et al., cond-mat/0308368)

…Should be measured on $Sr_{0.5}V_6O_{15}$ and $Sr_1V_6O_{15}$ single crystals

ARPES measurements have been done in Nancy[1] with a UV lamp and a high resolution SES-200 analyzer and at LURE[3] with a synchrotron radiation source. XPS, χ(T) and ρ(T) data have been measured in Nantes[2].