MAGNETIC SUSCEPTIBILITY IN THE INSULATING AND METALLIC PHASES OF VO₂: THE CONTRIBUTION OF ELECTRON-ELECTRON AND ELECTRON-LATTICE INTERACTIONS

P. Leroux-Hugon, D. Paquet

To cite this version:


HAL Id: jpa-00219948
https://hal.archives-ouvertes.fr/jpa-00219948

Submitted on 1 Jan 1980

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.
MAGNETIC SUSCEPTIBILITY IN THE INSULATING AND METALLIC PHASES OF VO₂: THE CONTRIBUTION OF ELECTRON-ELECTRON AND ELECTRON-LATTICE INTERACTIONS.

P. Leroux-Hugon and D. Paquet*

C.N.R.S. - 1 place A. Briand, 92190 Meudon-Bellevue, France.
* C.N.E.T. - 196, rue de Paris, 92220 Bagneux, France.

Résumé.- Nous présentons une analyse de la transition de phase VO₂, basée sur un développement de l'énergie libre en fonction de deux paramètres, l'amplitude de la distorsion de réseau et l'amplitude du moment magnétique local moyen ; cette analyse incorpore donc à la fois l'interaction électron-électron et l'interaction électron-réseau. On discute les implications de ces mécanismes pour la susceptibility magnétique.

Abstract.- We present an analysis of the VO₂ phase transition based upon a free energy expression which depends on two parameters, the amplitude of the lattice distortion and the amplitude of the average magnetic local moment; this analysis thus incorporates both electron-electron and electron-lattice interactions. Bearing of these mechanisms on the magnetic susceptibility are discussed.

Vanadium dioxide undergoes at 340 K a first order crystallographic phase transition /1,2,3/. The opening of a gap, and the onset of localized magnetic moments on Vanadium atoms in metastable phases is understood as a consequence of electron-electron correlations, whereas electron-lattice interactions, associated with some strong nesting of the Fermi Surface /3/ account for the crystallographic symmetry breaking. (Tetragonal to monoclinic).

We present a model of the phase transition which incorporates both mechanisms on the same footing and which is tested on its predictions regarding the temperature dependence of the magnetic susceptibility. Calculations being rather intricate, we shall only discuss the physical basis of the model, outline the methods used to elaborate the thermodynamics, and give some results. A complete discussion will be given elsewhere.

Experiments show that the metallic phase is paramagnetic, with a Pauli-like susceptibility which is enhanced and decreases with increasing temperature, and that the distorted insulating phase displays a vanishing susceptibility. A pure electron-electron correlations mechanism (Hubbard) would qualitatively account for the susceptibility of the metallic phase, but would predict the existence of well developed local magnetic moments in the insulating phase exhibiting a Curie-like susceptibility. On the other hand, a pure electron-lattice mechanism (Peierls) would imply a normal Pauli susceptibility in the metallic phase, a diamagnetic behaviour in the insulating one, and could not account for the onset of local moments in the new insulating monoclinic phase obtained by chromium doping or under uniaxial stress /2/.

In the metallic phase, the Fermi levels falls in between two overlapping bands: i) a d// narrow one essentially made of Vanadium d-orbitals hybridized along chains parallel to the tetragonal axis, accommodating two electrons by V atoms and ii) a larger î one, corresponding to the hybridization of V d-orbitals with oxygen p-ones, accommodating four electrons. These two bands share one conduction electron.

The crystallographic distortion is described by a normal mode, associated to the K point of the tetragonal Brillouin zone (nesting vector of the Fermi surface), the static amplitude of which, labelled η, is the order parameter of the phase transition, and corresponds to a pairing of V atoms along chains, altogether with a tilt of these chains perpendicular to their axis.
The hamiltonian of the model writes:
\[ H = H_{d//}(n) + H_{d//}(n) + H_{ee} + H_{\text{lat}}(\eta) \]

\[ H_{d//}(n) \text{ and } H_{d//}(n) \text{ correspond respectively to the energy of non interacting } d_// \text{ or } d_// \text{ electrons subjected to the static distortion } \eta \text{ which} \]

(i) distorts the shape of the \( d_// \) density of states (Peierls mechanism), due principally to its pairing component.

(ii) increases (respectively decreases) the energy of the center of the gravity of the \( d_// \) (respectively \( d_// \)) band, due principally to the tilt component.

\( H_{ee} \) is the hamiltonian describing electron-electron interactions on the same \( V \) atom,.

Three terms appear: \( d_// - d_//, d_// - d_// \) and \( d_// - d_// \) interactions.

\( H_{\text{lat}} \) is the potential energy of the normal mode.

The \( d_// - d_// \) and \( d_// - d_// \) interactions are handled in the mean field approximation and induce only a dependence of the center of gravity of the bands on their mutual filling. The larger \( d_// - d_// \) interaction is accounted for using the self-consistent alloy analogy of the Hubbard model /4/.

The intra-site term:
\[ H_{d//} = U \frac{1}{4} \sum_{i} n_{i}^{+} n_{i}^{-} \]
where \( n_{i}^{+} \) stands for the occupation number operator for spin \( + \) electrons on site \( i \), writes:
\[ H_{d//} = U \frac{1}{4} \left\{ (n_{i}^{+} n_{i}^{+})^{2} - (n_{i}^{+} n_{i}^{-})^{2} \right\} \]
which is transformed into
\[ H_{d//} = U \frac{1}{4} \left\{ 2n_{i}^{-} (n_{i}^{+} n_{i}^{+} - 2n_{i}^{+} n_{i}^{-} + n_{i}^{-} + 1) \right\} \]
where \( n_{i} = n_{i}^{+} + n_{i}^{-} \), \( \eta_{i} = n_{i}^{+} - n_{i}^{-} \) are supposed to be static. We assume

(i) no charge fluctuation, i.e. \( n_{i} = n_{0} \)
(ii) \( \eta_{i} = \epsilon_{i} u \) where \( \epsilon_{i} = \pm 1 \) with probability \( 1/2 - 1/2 \); \( u \) being the average amplitude of the local moments.

(iii) The correlation between \( \eta_{i} \) to be described in terms of an Ising model with exchange interactions only between nearest neighbours along a chain, whose value depends only on \( U \) and on the electronic hopping integrals, which themselves vary with \( \eta \). The exchange integrals are estimated within an hydrogen molecule model /2/.

\( d_// \) electron hamiltonian is thus transformed into the hamiltonian of non interacting electrons propagating in an uncorrelated static alloy, and a corrective term (Ising) describing the correlations between local moments. The density of states of \( d_// \) electrons is then found using the Coherent Potential Approximation /5/; the random potential on the sites is simulated by an energy dependent one \[ ], the same on each site, which defines an effective medium. The self-energy \( \Sigma \) is chosen from the prescription /5/ that a single scatterer (i.e local moment) embedded in the effective medium should produce no further scattering on the average. The CPA equations are:
\[ \Sigma = \left( \frac{U}{2} \right)^{2} F(z) \]
where
\[ F(z) = \int_{-1/2}^{1/2} \frac{d\mu}{z - \mu} \]

\( z \) is the Green function at energy \( z \), \( \rho \) being the unperturbed density of states. The actual density of states becomes \( \tilde{\rho}(E) = \frac{1}{2} \text{Im} F(z) \).

For each value of \( \eta, \mu \) and the temperature \( T \), a density of states configuration and a free energy \( \mathcal{F}(\eta, \mu) \) is calculated. The equilibrium state is found by minimizing \( \mathcal{F} \) with respect to \( \eta \) and \( \mu \). The free energy surface \( \mathcal{F}(T, \eta, \mu) \) is displayed on figure 1 at the transition temperature. The two separate equal minima correspond to the two equistable states coexisting at the first order transition. The metallic state \( M \) corresponds to no distortion and a small moment \( \mu \approx 0.3 \). The distorted insulating state \( I \) \( (\eta = 0.11, \mu = 1.0) \) displays a splitting of the \( d_// \) band, due to interelectronic correlations. Figure 2 shows the temperature variation of the self-consistent mean amplitude of the average local moment \( \mu \) and of the nearest neighbour intradimer (I) and extradimer (X) spin correlation function \( \langle \epsilon_i \epsilon_{i+1} \rangle \). We find, in the insulating phase a complete antiferromagnetic order between local moments in a dimer, which produces a vanishing susceptibility.

In the metallic phase the local moments
are not well developed. The susceptibility cannot be calculated from the Ising chain (which supposes rigid amplitude of local moments and only changes in the correlation functions), but must be derived from the alloy analogy. Under application of a magnetic field, the symmetry in the variational statistical distribution of the scatterers is broken. The latter becomes:

\[
\begin{align*}
\mu_+ &= \mu + \Delta \mu & \text{if } \mu > 0 \text{ with probability } p_+ = \frac{1}{2} + \Delta \mu \\
\mu_- &= \mu - \Delta \mu & \text{if } \mu < 0 \text{ with probability } p_- = \frac{1}{2} - \Delta \mu
\end{align*}
\]

the two functions \(\Delta \mu\) and \(\Delta \mu\) vanishing at zero field.

Under such conditions, electrons \(+\) and \(-\) propagate into two different alloys corresponding to different self-energies (\(\mathcal{F}_+\) and \(\mathcal{F}_-\)) and Green functions (\(F_+\) and \(F_-\)). The total free energy must be calculated for a given statistical distribution:

\[
\mathcal{F} = \mathcal{F}_0 + \Delta \mathcal{F} (\mu, \Delta \mu, \hbar)
\]

Minimizing \(\mathcal{F}\) versus \(\Delta \mu\) and \(\Delta \mu\) gives \(\Delta \mathcal{F} = -\frac{1}{2} \chi \hbar^2\) where \(\chi\) is the magnetic susceptibility. Note that \(\chi\) is neither the addition of a Pauli susceptibility of free electrons and a Curie susceptibility of local moments, nor is it simply given as a correlation-enhanced Pauli one:

\[
\chi = \frac{\chi_0}{1 - \frac{U}{2 \mu B} \frac{\Delta p}{\Delta \mu}}
\]

because (i) the density of states depends on \(\mu\), (ii) exchange interactions between moments would lower the enhancement factor and (iii) it is necessary to account for the large amplitude of the local moment thermal fluctuations. One may include this latter effect by writing:

\[
\Delta \mathcal{F} = \Delta \mathcal{F}_0 + \frac{K T}{3 \mathcal{F}} \frac{\delta^2}{\delta \mu^2} (\Delta \mathcal{F})
\]

where \(\Delta \mathcal{F}\) does include fluctuations and \(\Delta \mathcal{F}_0\) does not. We have performed the calculation of \(\Delta \mathcal{F}\), limiting ourselves to no change in concentration (\(\Delta c = 0\)) and including the exchange interaction specified by \(J\).

---

**Fig. 1:** Free energy versus the amplitude of the distortion \(\eta\) and the mean amplitude of the average local moment \(\mu\), calculated at the transition temperature. The two equal minima \(M\) and \(T\) correspond to the metallic undistorted phase, and the insulating distorted one.

**Fig. 2:** Temperature variations of the mean amplitude of the average local moment \(\mu\), and of the nearest neighbour intradimer (I) and extradimer (X) spin correlation function \(\langle e_i e_{i+1} \rangle\).

This leads, for a single band, to:

\[
\chi = \frac{\phi}{1 - \frac{U}{2 \mu B} \frac{1}{1 + \frac{4 \phi}{U}}} - \frac{1}{2 \mu B} \frac{1}{1 + \frac{4 \phi}{U}}
\]

where \(\phi = X_p + \frac{K T}{3 \mathcal{F}} \frac{\delta^2}{\delta \mu^2} X_p\).
\( \chi_P \) being the Pauli susceptibility associated to the \( \nu \)-dependent density of states. This susceptibility calculation has to be performed for both the \( d \parallel \) and \( s^* \) bands, yielding \( \chi_{\text{tot}} = \chi_{d \parallel} + \chi_{s^*} \). Numerically we find:

\[
\begin{align*}
\chi_{\text{tot}} (340 \text{ K}) &= 4.30 \times 10^{-4} \text{ emu/mole} \\
\chi_{\text{tot}} (900 \text{ K}) &= 3.74 \times 10^{-4} \text{ emu/mole}
\end{align*}
\]

accounting, qualitatively, for both the discontinuous increase of \( \chi \) at the transition and for its temperature dependence. Note that, although the two susceptibilities are added in \( \chi_{\text{tot}} \), the \( \frac{2\pi}{\hbar^2} \) term, depending on the actual filling of the two bands, accounts for their mutual electrostatic interaction.

References