The Electronic Structure of the Ti_4O_7 Magneli Phase

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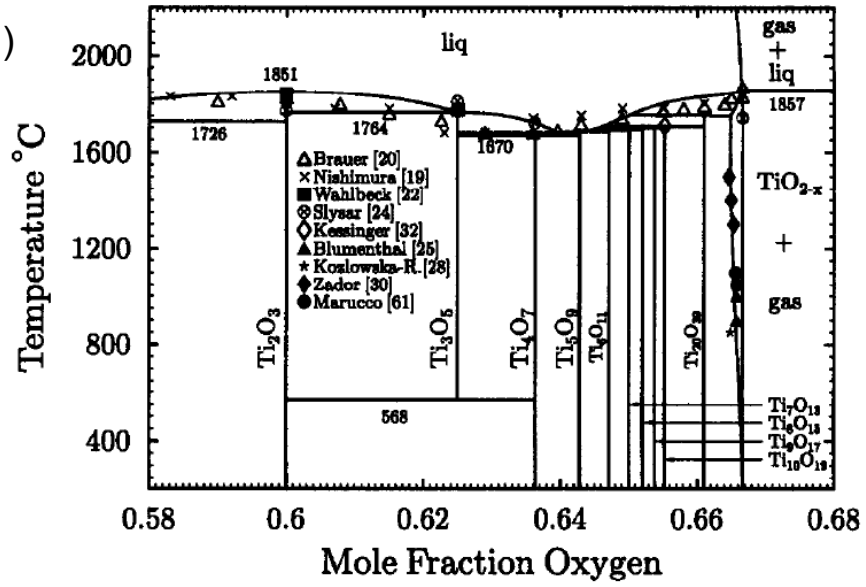
Magneli Phases

1)



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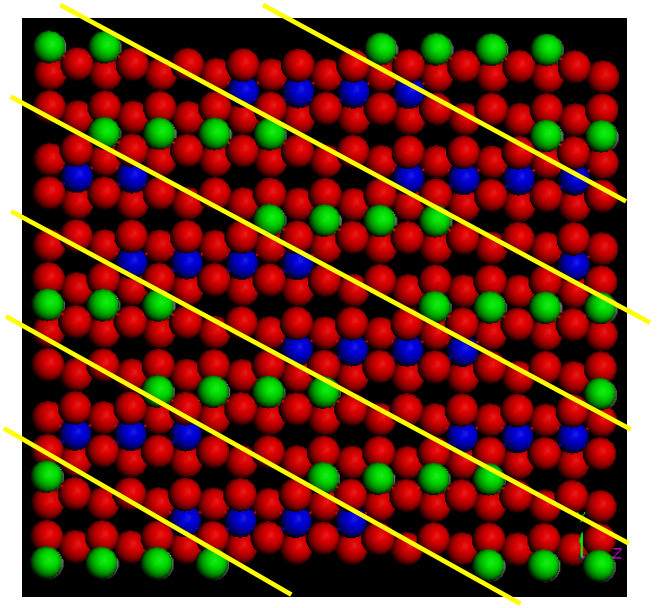


Metal nets in antiphase. $(121)_r$
Cristallographic shear plane.

T_nO_{2n-1} composition. For n between 3 and 9 shear planes are the (121).

Ti_4O_7 is a semiconductor at T<120K semicond. with 0.25eV band gap[(1)].

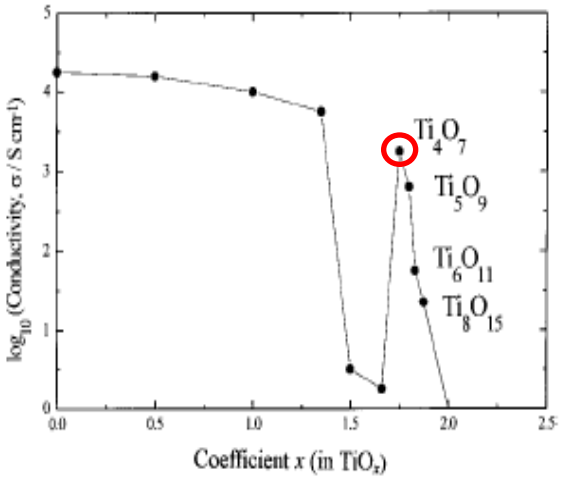
T_4O_7 Metal-semicond. transition at ~150K, semicond-semicond. trans. at T~135K.

(1) D. Kaplan *et al*., Philosophical Mag., Vol. 36, pp. 1275, 1977.

(2) P. Waldner and G. Eriksson, Calphad Vol. 23, No. 2, pp. 189-218, 1999.

Ti_4O_7 Magneli Phase: Electric and Magnetic properties

1)



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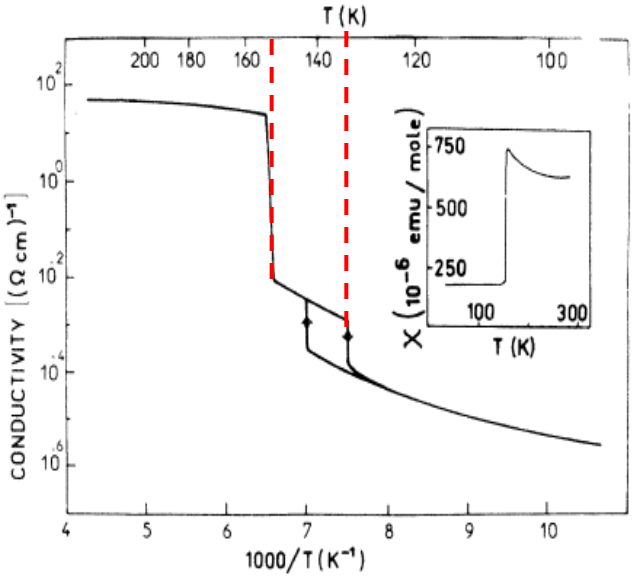


Conductivity of Ti_4O_7 single crystals

- Ti4O7 conductivity is higher than the graphite one.
- 3 well-differentiated phases.
- semicond-semicond and semicond-metal transitions.
- Exp. Evidence suggests: Charge localization on the Ti atoms changes at every phase.

Material	Resistivity (μΩ-cm)
Copper	1.7
Ti_4O_7	500
Graphite	1375

Table (1)

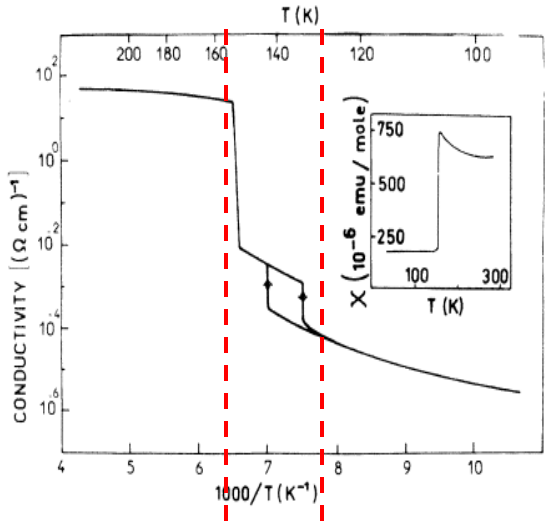
1) J. R. Smith *et al*, J. Appl. Electroch., **28**, pp 1021, (1998).

2) S. Lakkis *et al*, PRB., **14**, pp 1429, (1976).

3) L. N. Mulay *et al*, J. of Appl. Phys., **41**, pp 877 , (1970).

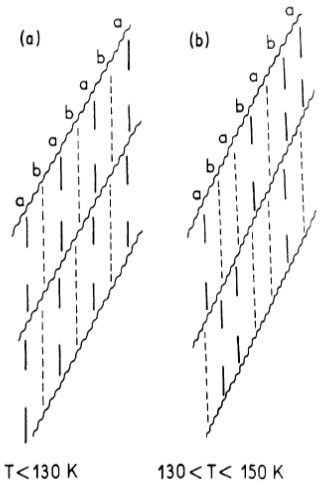
Ti_4O_7 Magneli Phase: The Bipolaron Model

1)



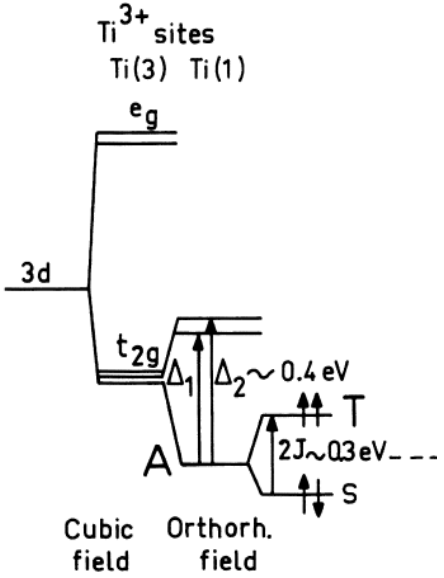
H.T.P. I.T.P. L.T.P.

2)



Charge distribution at low and intermediate T

3)



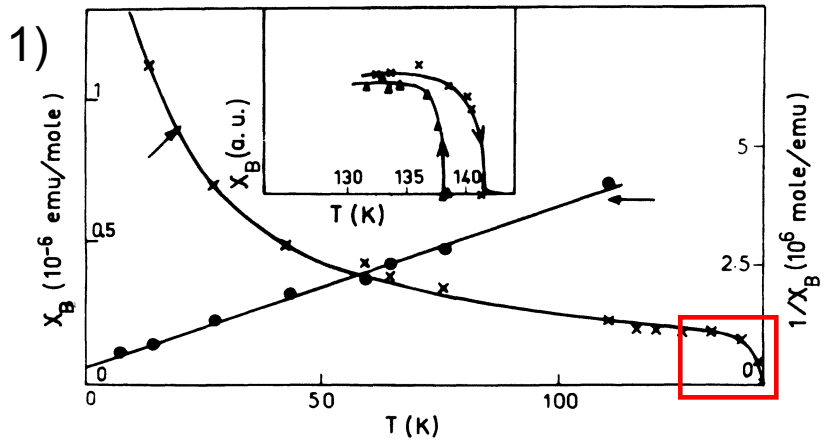
- Ti-Ti pairs: small on-site localised bipolarons, which are bound states of two Ti+3 ions stabilised by a lattice distortion.
- In the low T phase the Ti 3d electrons forming the bipolarons were paired in non-magnetic bonds. The bipolarons were ordered.
- In the intermediate temperature phase the bipolarons disordered.
- In the high temperature phase the bipolarons dissociated and the 3d electrons delocalized.

1) M. Marezio *et al*, J. Solid. St. Chem., **6**, pp 213, (1973).

2) S. Lakkis *et al*, PRB., **14**, pp 1429, (1976).

Ti_4O_7 Magneli Phase: The Bipolaron Model Drawbacks

- No intrinsic EPR signal in the bipolaron model.



Intensity of the EPR signal as a function of T.

- New model for the 140K phase.

This structure shows long range order: the bipolarons are still present, but they are not disordered (Reference (1)).

1) Y. Le Page *et al* , J. Solid St. Chem., **53**, pp 13, (1984).

2) S. Lakkis *et al*, PRB., **14**, pp 1429, (1976).

Ab inito calculations

CRYSTAL

Hybrid density functional: B3LYP,
GGA Exchange
GGA Correlation
20% Exact Exchange

Local basis functions: atom centred Gaussian type functions.
Ti: 27 atomic orbitals, O: 18 atomic orbitals

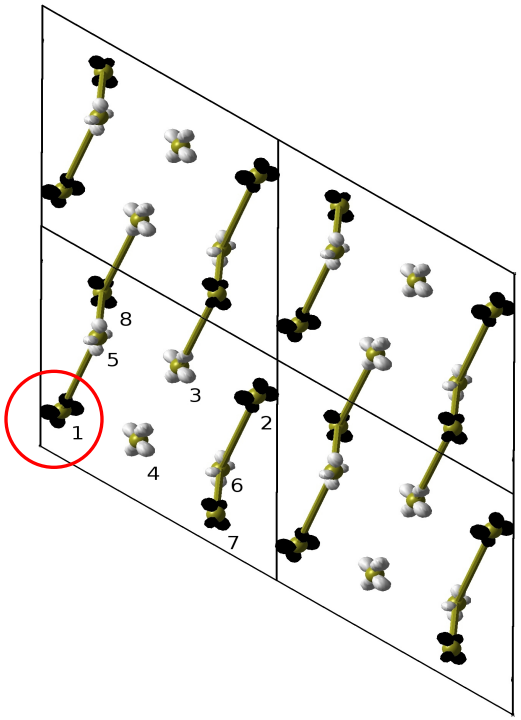
Supercell approach.

Ti_4O_7 structures at the low, intermediate and high temperature phases taken from M. Marezio *et al*, J. Solid. St. Chem., **6**, pp 213, (1973).

Ti4O7 structure at the different phases taken from Y. Le Page *et al* , J. Solid St. Chem., **53**, pp 13, (1984).

Ti_4O_7 low and high T structures from Marezio et al (1).

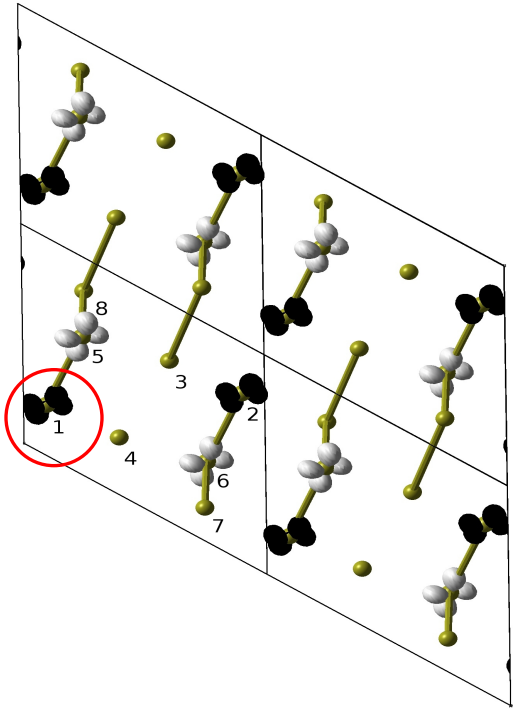
298 K



Ti atom	$\mu = n_\alpha - n_\beta$	
	298 K	**120 K**
1	-0.4491	-0.8722
3	0.4199	0.0259
5	0.3311	0.8748
7	-0.3027	-0.0387

Ti t_{2g}-like spin population in bohr magnetons

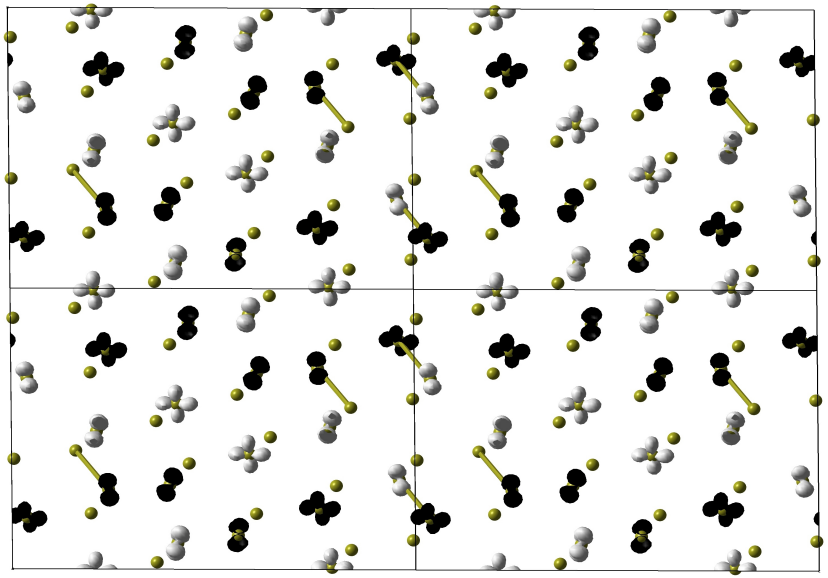
120 K

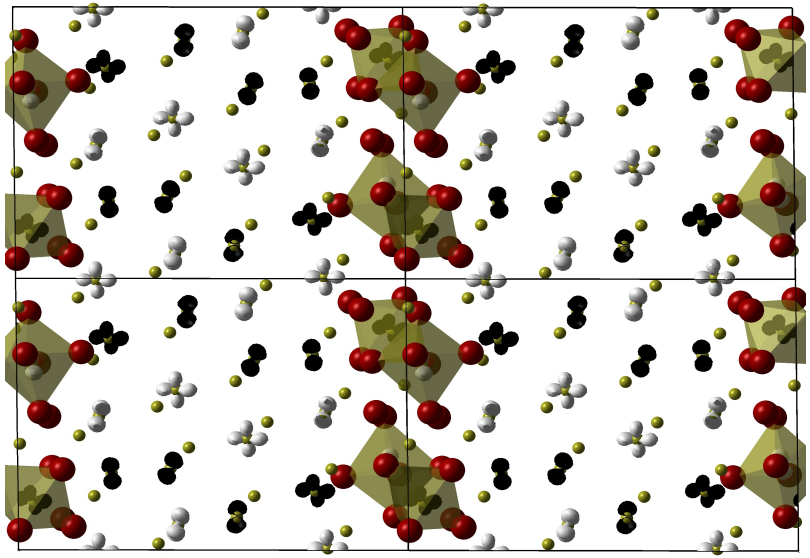


- At 120K the spin localises in Ti^{+3} t_{2g}-like orbitals which are antiferromagnetically coupled forming dimmers.
- At 298K the electrons delocalise.

(1) M. Marezio *et al*, J. Solid. St. Chem., **6**, pp 213, (1973).

Ti_4O_7 intermediate T structure from Le Page et al (2)





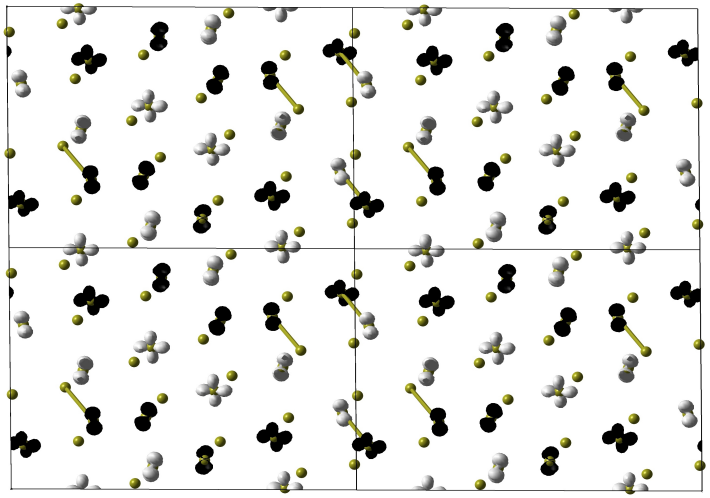
Ti atom	$\mu = n_\alpha - n_\beta$		
	120 K	**140 K**	**298 K**
Ti ↑	0.8748	0.788	0.4199
Ti ↓	-0.8722	-0.751	-0.4491

- At 140 K the spin is localised in Ti^{+3} t_{2g}-like orbitals. Only a subset of these Ti+3 ions form antiferromagnetically bonded pairs.
- The 140 K electronic structure is not a bipolaronic state: there is a mixture of polarons and bipolarons.

(2) Y. Le Page *et al* , J. Solid St. Chem., **53**, pp 13, (1984).

Interpretation of magnetic measurements

Susceptibility measurements

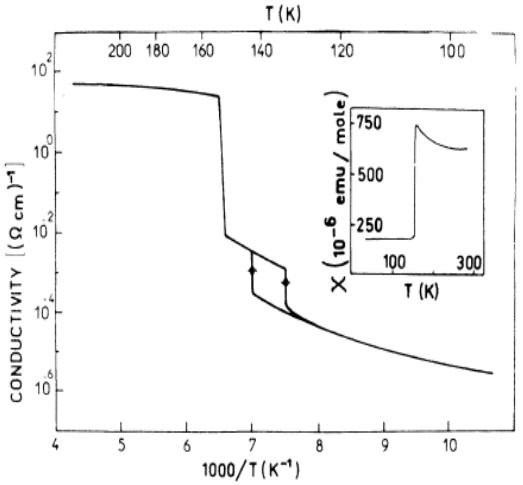


a) Ferromagetic.

b) Flip the spin of half of the elctrons forming bipolarons.

c) Flip the spin of half of the electron forming polarons.

Lowest energy for change:
0.1 eV per Ti_4O_7 unit.



EPR measurements

Ti atom	$\mu = n_\alpha - n_\beta$		
	120 K	**140 K**	**298 K**
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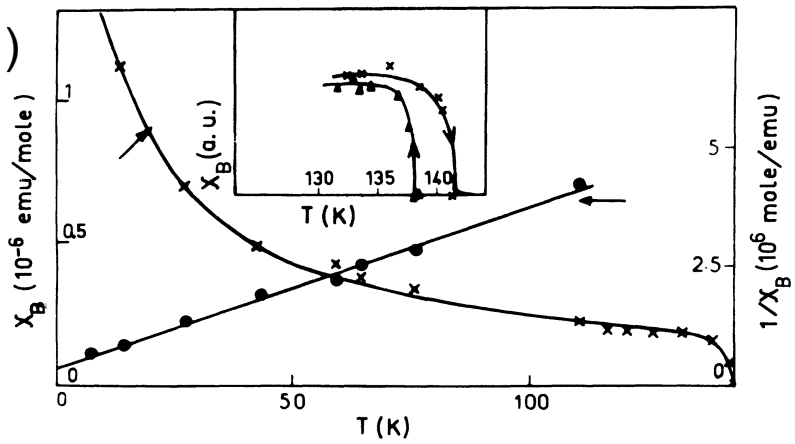
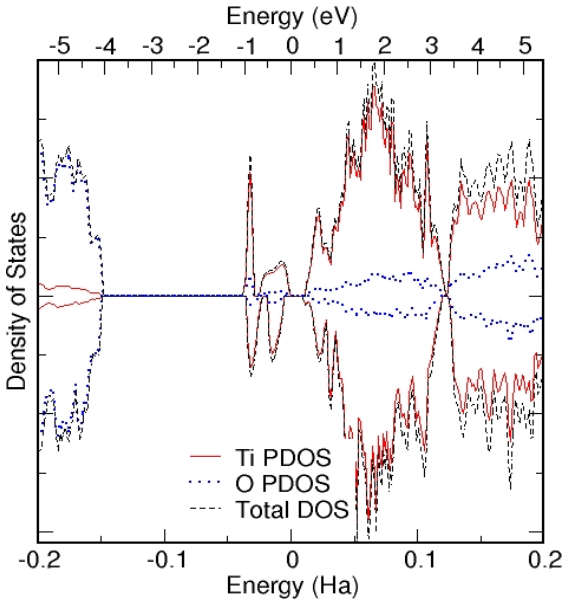
1)



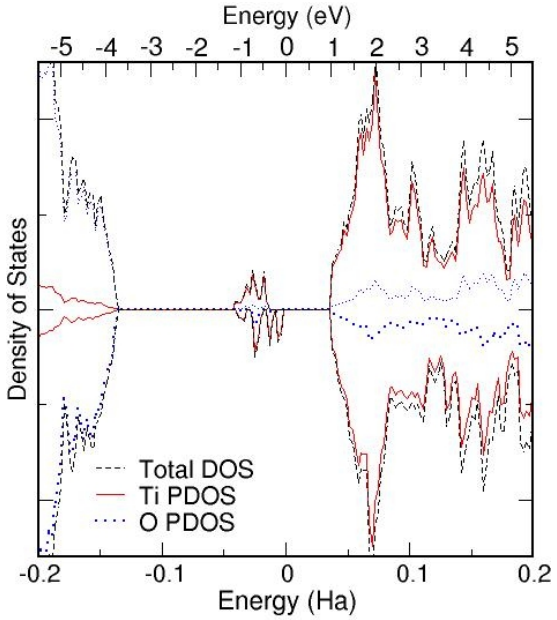
Intensity of the EPR signal as a function of T.

Ti_4O_7 low, intermediate and high T DOS.

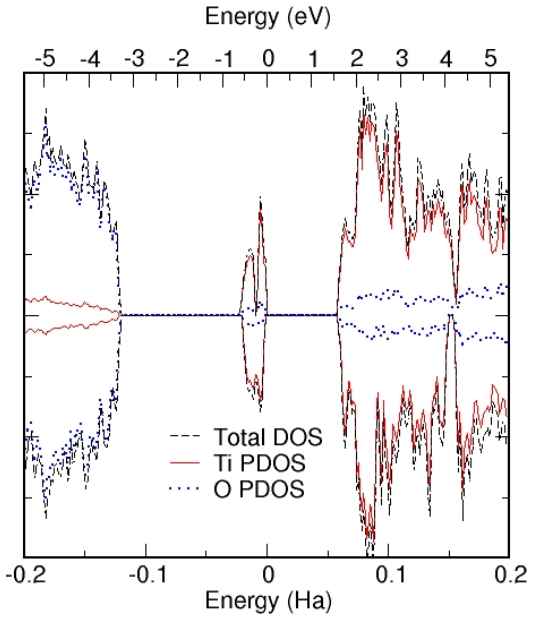
298 K



140K



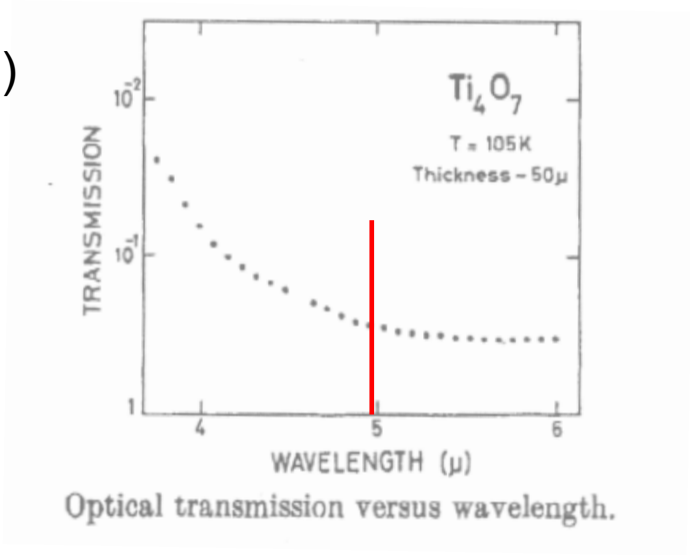
120 K



(1) L. Liborio *et al*, PRB., **79**, pp 245133, (2009).

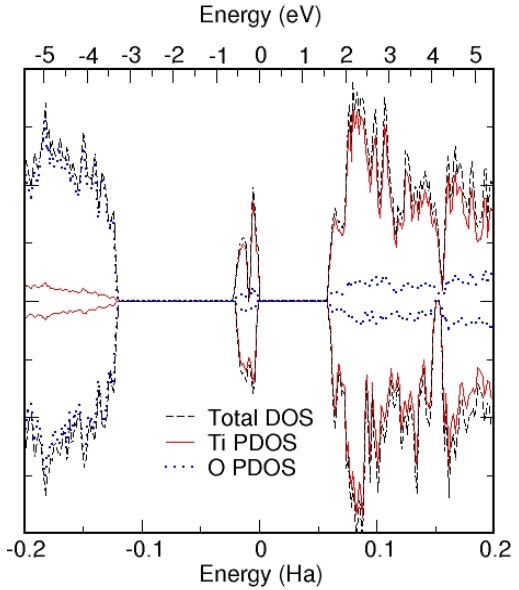
Ti4O7 low T DOS and optical properties

1)



Optical transmission versus wavelength.

2)



DOS for T<120K

Methodology	LTP Band Gap (eV)
Optical Abs. (1)	0.25
PES + XAS (4)	0.04

Is the theoretical band gap reasonable?

Some proposed absorption mechanisms:

- Spin flipping: Antiferro-Ferro

$E(120K)_{Ferro}$-$E(120K)_{Antiferro}$ = 0.3 eV

- Infrared active phonon modes

1) D. Kaplan *et al,* Phil. Mag., **36**, pp 1275, (1977).

2) S. Lakkis *et al*, PRB., **14**, pp 1429, (1976).

3) L. Mulay et al, J. of Appl. Phys., **41**, 877, (1977).

4) M. Abbatte et al, PRB, **51**, 10150 (1995).

Conclusions

- We propose an alternative interpretation of the Ti_4O_7 electronic structure.
- The Ti_4O_7 120K phase is an antiferromagnetic charge-ordered semiconducting state.
- The Ti_4O_7 120K phase is a bipolaronic state, but the bipolarons are NOT covalently bonded: the spin localises in t_{2g}-like orbitals belonging to Ti^{+3} ions, and these ions are antiferromagnetically coupled.
- According to our calculations, in the new ordered structure for the 140 K phase, spin localises in Ti^{+3} t2g-like orbitals. But the 140K state is not a bipolaronic state: there is a mixture of polarons and bipolarons.
- In the 298K phase electrons delocalise and spin moments decrease their value.
- Our results provide a sensible explanation for the behaviour of the magnetic susceptibility and EPR measurements with temperature.
- Our results might be providing a sensible value for the fundamental band gap at low T.

Acknowledgements

Giuseppe Mallia

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Keith Refson

Barbara Montanari