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	Experiment title:	**Experiment number:**
![ESRF logo] **ESRF**	**Is the metal-insulator transition in VO$_2$ a classical Peierls transition?**	HE-1550
Beamline: ID08	**Date of experiment:** from: 04-02-2004 to: 10-02-2004	**Date of report:** 26-02-2004
Shifts: 18	**Local contact(s):** Nick Brookes, Federica Venturini	*Received at ESRF:*

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Remarks: During the 04-02-2004 to 10-02-2004 period, we have studied the metal-insulator transition (MIT) phenomenon in VO$_2$, see Report 1. We have also spent time on GdBaCo$_2$O$_{5.5}$, a new type of layered cobaltates currently under intense debate because the MIT is suspected to be accompanied by a spin-state transition, see Report 2.

Report 1: Metal-Insulator Transition in VO$_2$.

VO$_2$ is a non-magnetic oxide that undergoes a metal-to-insulator transition (MIT) at 340 Kelvin or 67° Celsius. Above this temperature, VO$_2$ is metallic and has the rutile (TiO$_2$) crystal structure (*R*-phase). At low temperatures, it is an insulator with a monoclinic structure (*M$_1$*-phase), in which V-V pairs are formed. A review about this material and its properties can be found in reference [1].

The long standing debate about this compound concerns the nature of the MIT. The issue is whether the non-magnetic insulating state should be regarded as a Peierls insulator with the character of a band insulator (one-electron picture) [2], or whether it should be viewed as a Mott-insulator (many-body picture) [3]. In other words, the importance of electron correlation effects in this lattice-coupled metal-insulator transition is at the heart of the discussion. Up to now, only very few photoemission studies have been reported in the literature, and Fig.1 shows the published valence band spectra.
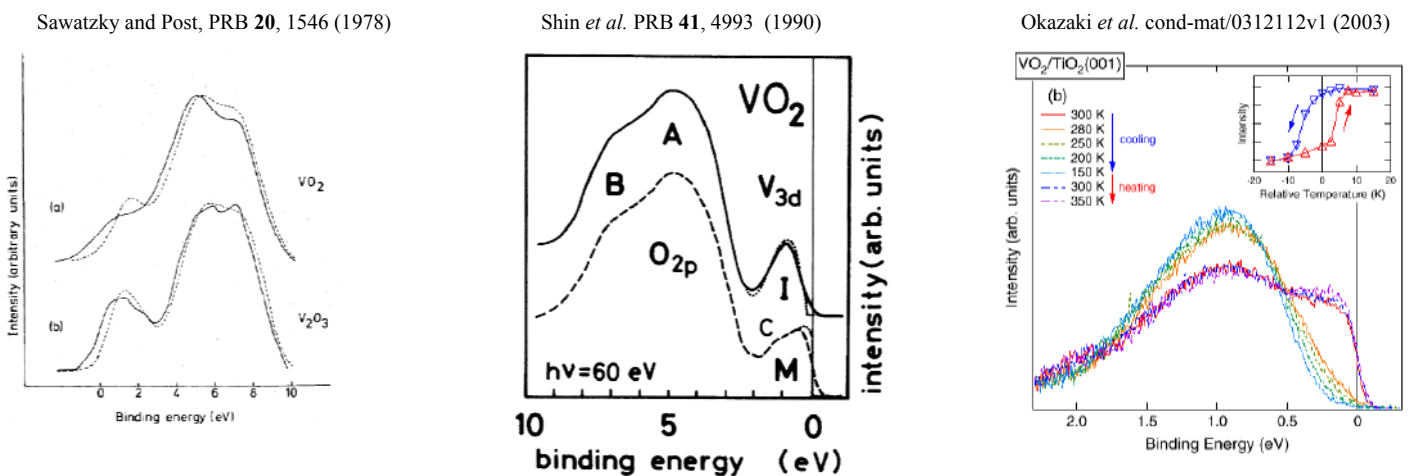

Fig 1: results from previous PES studies on VO$_2$ reported in the literature

At ESRF we have carried out *bulk sensitive* valence band photoemission measurements on single crystals of VO_2 with an overall energy resolution of 150 meV. The results are shown in Fig.2a. One can directly see that the spectra are quite different from the data reported in the literature as depicted in Fig.1. Our spectra show a substantially more dramatic change in the spectral line shape across the MIT. Especially in the metallic phase we have a lot more spectral weight at the Fermi level than the corresponding spectra of the literature. Bulk sensitivity is here the key issue: the fact that the measurements have to be carried out at somewhat elevated temperatures, e.g. 90° Celsius in order to be sufficiently above the MIT temperature of 67° Celsius, may cause the near surface region of the VO_2 crystal to suffer some loss of oxygen, since the most stable ionic form of vanadium is V^{3+} and not V^{4+}. To obtain the reliable data, we have (1) used single crystals, (2) measured them at normal emission, and (3) used the relatively high photon energy of 700 eV to obtain a reasonable escape depth for the valence band photoelectrons. The use of high photon energies has also other important advantages as compared to the use of the more common ultra-violet light: the high kinetic energies of the valence band photoelectrons will reach final states that are very much free electron like, and the matrix elements for the photoemission transitions becomes much simpler, meaning that the interpretation of the spectral lineshapes and intensities becomes much more transparent. One now really measures the V 3d spectral weight (the O 2p photoionization cross section is relatively small) and has direct information on the one-hole Green's function of the system that can be compared straightforwardly to the theoretical predictions.
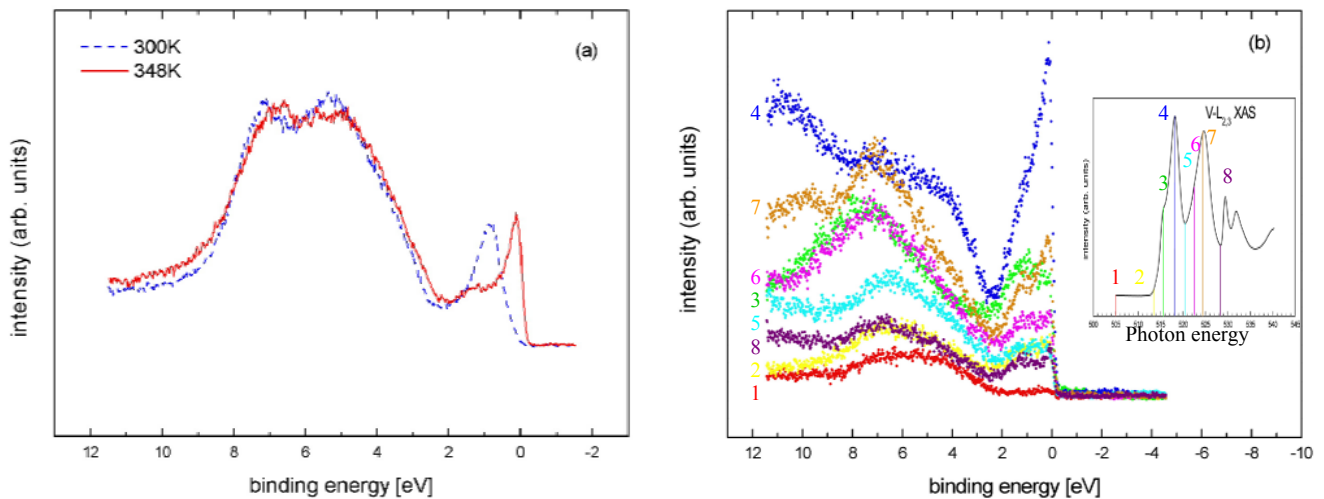

Fig 2: results of our measurements on VO_2 during the experiment HE-1550 at the ESRF

The most relevant result as shown in Fig. 2a., is that for the first time we now have a clear view on the line shape of the valence band of the metallic phase. At the Fermi level the spectral weight is extremely high, and at 1.2 eV binding energy it is low but not zero. This last aspect is important if one makes a comparison to the LDA calculations [2,4]: these one-electron calculations predict the existence of a gap between the V 3d and the O 2p DOS of the valence band, and experimentally this is clearly not the case. This indicates that the 1.2 eV structure should be ascribed to a many-body effect, i.e. analogous to the famous 6 eV satellite in Ni metal. One can then also label the intense Fermi spectral weight as the coherent peak, and the 1.2 eV structure as the incoherent peak. Support for these assignments can be found from the resonant photoemission data as shown in Fig. 2b. One can clearly observe that the intensity enhancements depend strongly on the photon energy, and that the dependence is different for the coherent and the incoherent peaks, which is typical for structures having different origins.

An important detail in Fig. 2a is that the energy position of the incoherent peak is different from that of the intense peak of the insulating phase. This was one of the major issues that Liebsch had [5]: using LDA+DMFT, Liebsch calculated that the incoherent peak of the metallic phase has never the same energy as the main peak of the insulating phase, while the recent spectra of Okazaki et al. seem to suggest that they have the same energy. Our data therefore now resolve this problem: we confirm that Liebsch is correct. Another exciting aspect is that very recently, at the DPG March Meeting in Regenburg, Liechtenstein *et al*. have presented their results using <u>cluster</u>/LDA+DMFT calculations which are in excellent agreement with the dramatic spectral weight transfer that we have measured across the MIT. This

to us confirms our ideas that the *k*-dependence of the self-energy is extremely crucial to understand the MIT and that therefore the standard LDA+DMFT will completely miss the point. By taking a cluster, however, one can account for the most relevant part of this *k*-dependence of the self-energy, namely the spin-spin correlation between nearest neighbor V ions in the dimers. Park and Tjeng [6] have inferred that similar effects are playing the essential role in the famous MIT of V_2O_3, namely that nearest-neighbor spin-spin correlations are switched across the MIT due to the switching of the local orbital occupations, with the results that effective band widths are strongly modified. In fact, an explicit cluster example is even given in the Park and Tjeng paper [6] to illustrate this mechanism. The possible importance of spin-spin correlations for the MIT has been explored early on by Bulaevskii and Khomskii [7].
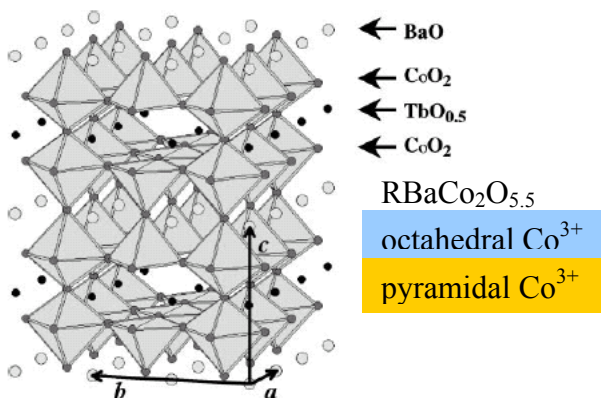
To summarize: The MIT in VO_2 is not a one-electron or band structure type of a Peierls transition. Strong electron correlations effects together with the Peierls dimerization are the crucial ingredients for the MIT in VO_2, in which dramatic changes in the nearest neighbor spin-spin correlation functions alter the effective band widths. A single band Hubbard model will not be sufficient to describe the MIT, because in our XAS experiments at the NSRRC-Taiwan we have also observed dramatic changes in the symmetry of the 3d t_{2g} orbital occupation across the MIT, thereby giving a natural explanation for the changes in the spin-spin correlation functions.
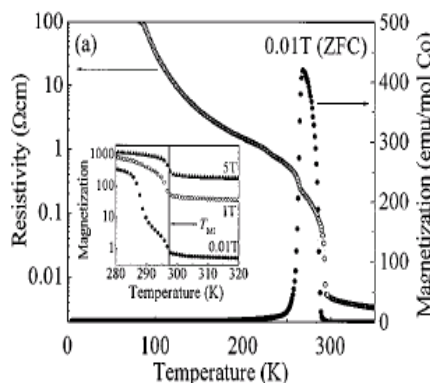
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Report 2: Metal-Insulator Transition in $GdBaCo_2O_{5.5}$.

The class of cobalt-oxide based materials has attracted considerable interest in the last decade because of expectations that spectacular properties may be found similar to those in the manganates and cuprates. Indeed, giant magneto resistance effects have been observed in the $La_{1-x}A_xCoO_3$ (A=Ca,Sr,Ba) perovskites and $RBaCo_2O_{5+x}$ (R=Eu,Gd) double perovskites. Very recently, also superconductivity has been found in the $Na_xCoO_2.yH_2O$ material. *A key aspect of cobalt oxides that distinguishes them clearly from the manganese and copper materials, is the spin state degree of freedom of the $Co^{3+/III}$ and Co^{IV} ions*: it can be low, intermediate and high (S=0,1,2 for $Co^{3+/III}$ and S=1/2,3/2,5/2 Co^{IV}) [1]. This aspect comes on top of the orbital, spin (up/down) and charge degrees of freedom that already make the manganese and cuprate systems so exciting. It is, however, also precisely this aspect that causes considerable debate in the literature.

Fig. 3. Crystal structure and properties of $RBaCo_2O_{5.5}$ (R = rare earth).

Giant magnetoresistance, metal-insulator transition (MIT), spin-state transition, and orbital-ordering have been reported to occur in $RBaCo_2O_{5.5}$ (R = rare earth) [2-7]. The basic structure of $RBaCo_2O_{5.5}$ consists of $RO_{0.5}$ and BaO layers alternative extending along the *c* axis with CoO_6 octahedra and CoO_5 pyramids alternatively extending along *b* axis, see Fig. 3. The MIT temperature depends on the R element, and is in the range of T_{MI} = 310 K- 360 K. The MIT is thought to be due to a spin-state transition from a low-spin (LS) to

an intermediate (IS) or a to high spin state (HS) of the Co^{3+} ions in the CoO_6 octahedra in analogy to $LaCoO_3$, while the Co^{3+} ions in the CoO_5 pyramidal sites are supposed to remain unchanged in the IS.

At ESRF we have carried out *bulk sensitive* valence band photoemission measurements on single crystals of $GdBaCo_2O_{5.5}$ with an overall energy resolution of 150 meV. The spectra taken at temperatures both below and above T_{MI} are shown in Fig.4a. We have also included the spectrum of $EuCoO_3$, a known LS Co^{3+} system. One can directly see that all the $GdBaCo_2O_{5.5}$ spectra are quite different from that of $EuCoO_3$, indicating that there is no LS component in $GdBaCo_2O_{5.5}$ at any temperature. Moreover, there are no major line shape changes in the spectra across the MIT. This should be contrasted to the case of $LaCoO_3$, where the spectra change dramatically as a function of temperature [8]. All these observations demonstrate that the claims for a spin state transition induced MIT in $GdBaCo_2O_{5.5}$ are simply wrong. To double check, we have also carried out detailed O-K (see Fig. 4b) and $Co-L_{2,3}$ (not shown here) measurements at the NSRRC in Taiwan. Also these data show no major changes across the MIT, again very much unlike $LaCoO_3$. In fact the XAS data very clearly show that all the Co^{3+} ions in $GdBaCo_2O_{5.5}$ are HS, not only above but also below T_{MI}. We are now very confident that all the assignments made so far in the literature for the Co^{3+} spin state are wrong and that we have to go back to the drawing board to find the mechanism of the MIT.
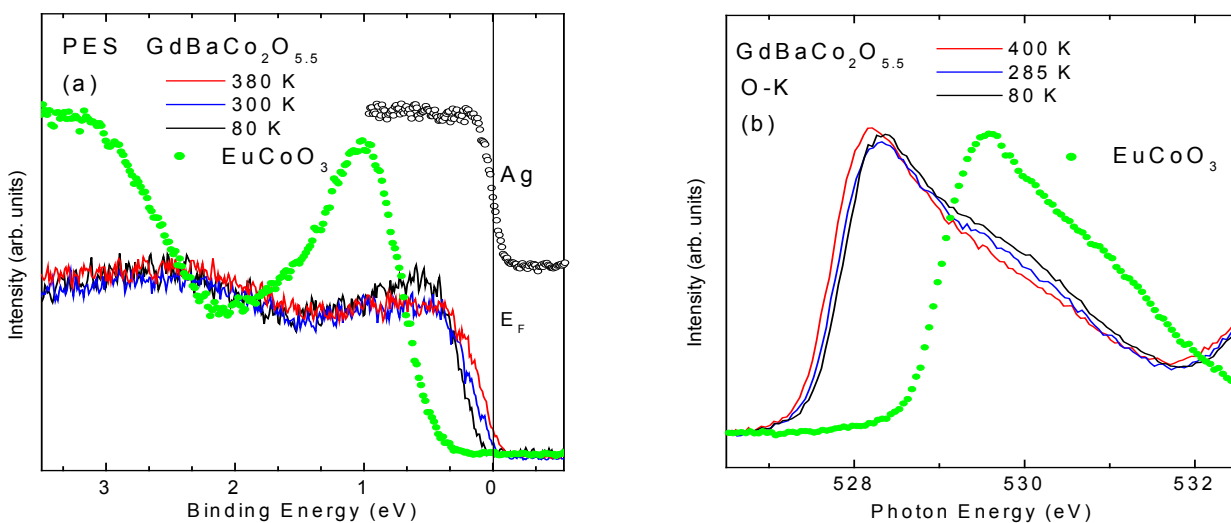

Fig. 4. (a) Valence band photoemission spectra taken at the ID08 beamline of the ESRF, and (b) O-K x-ray absorption spectra taken at the NSRRC-Taiwan.

A more detailed look into Fig. 4a reveals that the $GdBaCo_2O_{5.5}$ spectral weight at the Fermi level is negligible for all temperatures, so that we have to conclude that the material is an insulator all the time, i.e. there is actually no *metal*-insulator transition at all. What happens is that the band gap is reduced when the temperature is increased: Fig. 4a shows that the top of the valence band moves up by about 70 meV in going from 80 K to 300 K, and by 50 meV from 300 to 380 K, while Fig. 4b reveals that the bottom of the conduction band shifts downwards by about 60 meV for 80 K to 300 K, and by 70 meV for 300 K to 380 K. So in total, the band gap is reduced by about 130 meV in going from 80 K to 300 K, and a further 120 meV from 300 K to 380 K. The origin for this continuous insulator-to-insulator transitions is at the moment not clear, but one is tempted to speculate that it may be related to some form of short-ranged magnetic order-disorder phenomena.

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