

NiO(111) electronic structure in the paramagnetic phase measured by ARPES with polarised synchrotron radiation

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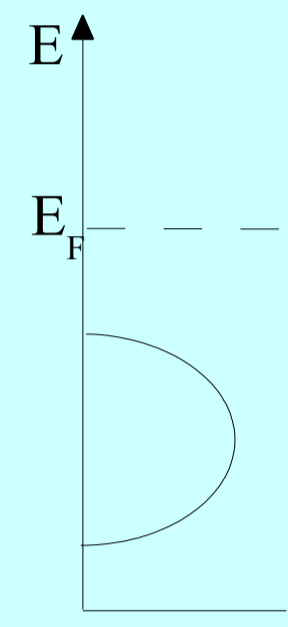
Introduction and Background

We present our ARPES data on a NiO(111) single-crystal. The reason of the work is twofold:

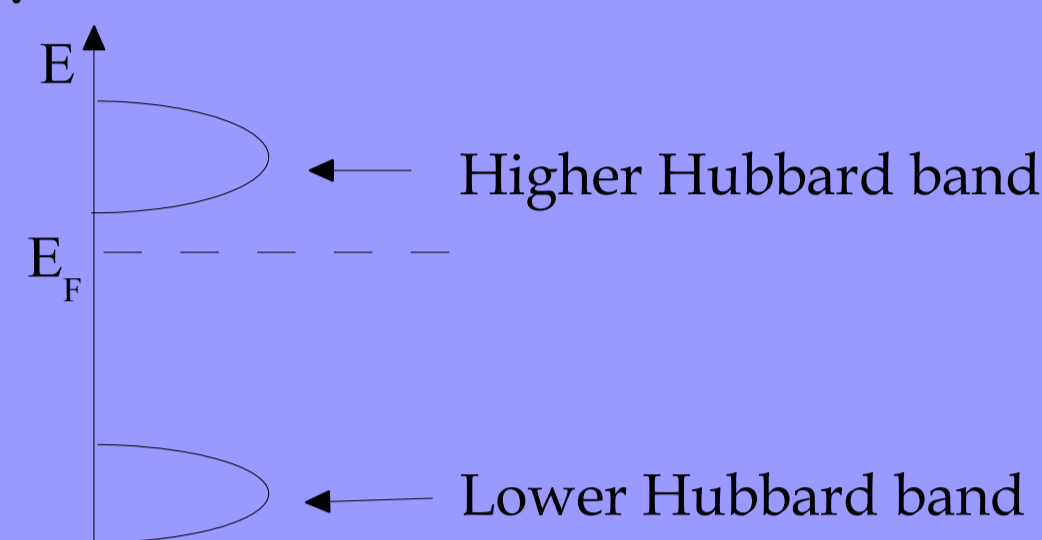
- 1) determining the electronic structure of the (111) surface;
- 2) investigating the metal-insulator transition.

The physics of NiO is determined by the strong interactions occurring between the Ni 3d electrons. In the ground state NiO is an **antiferromagnetic Mott insulator**.

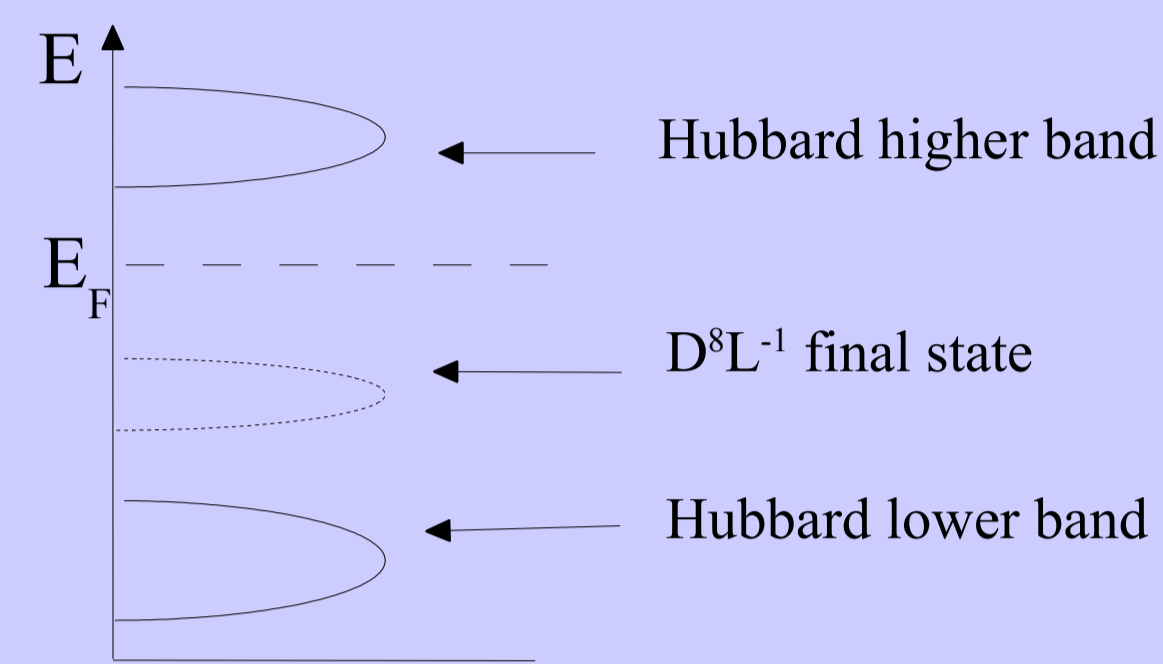
In a Bloch insulator or in a semiconductor there is a gap because there are as many bands as electrons in the outer atomic shells. The electrons then fill all the bands without reaching the Fermi level.



In a **Mott insulator** the Coulomb repulsion $U \sim 10\text{eV}$. This would stop the Ni electrons movement, if they had no kinetic energy. The partially filled Ni 3d bands split in two, called Hubbard sub-bands, one completely filled and the other completely empty.



In fact NiO, is a **charge-transfer insulator**, a special Mott insulator in which the lowest-lying excitation involves an electron transfer in the final state from the occupied ligand, oxygen, band to the metal empty band.



This picture is correct at low temperatures, but at high temperature the thermal excitations help the electron hopping between the ions. NiO is supposed to become a metal at high temperatures. In fact at T_N , the antiferromagnetic-paramagnetic transition temperature, NiO undergoes a **metal-insulator transition**. Since the metallicity of the system, its bands should cross the Fermi level and it should possess a **Fermi surface**. In general the density of states at E_F level should be different from zero.

Experimental

Two problems are related to ARPES on NiO: the surface preparation and the charging effects.

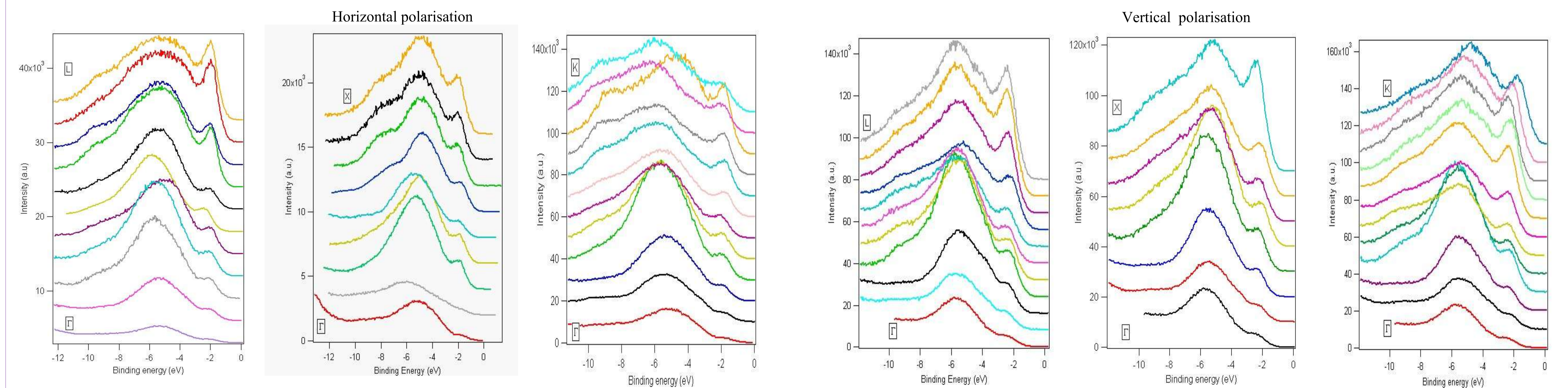
1) The preparation is crucial for photoemission experiments for the extremely short photoelectron elastic mean free path enhances the surface sensitivity of the technique. Experiments on the NiO(100) were carried out after cleaving the crystals. This exposes a fresh surface to vacuum but also, since there are three equivalent (100) planes, cracks it along the other planes generating structural defects. As other drawback, cleavage does not preserve the stoichiometry, increasing the defect density. It is reported that cleaved NiO(100) surfaces can lose up to 20% of their oxygen content. This improves the electron conduction and induces a density of states at E_F even in the insulating phase: a bright contradiction.

The (111) surface can not be cleaved because of the extremely low free energy. On the contrary annealing at 1000K under 10^{-5} mbar of oxygen completely removes contaminants, preserves the stoichiometry and maintains the crystal structure, as revealed by LEED.

2) As a general principle to a higher crystal quality correspond stronger intrinsic properties. One then expects that charging will appear in well-ordered insulating crystals. Ours, having a 0.02° of mosaic spread, was strongly insulating at room temperature, while cleaved crystals were conductive, at the same temperature, because of defects. To do ARPES we heated at 450°C , well above $T_N=263^\circ\text{C}$, which is also the metal-insulator transition temperature.

Our measurements are not influenced by the magnetic order, but they should show the Hubbard sub-bands joining according to the classical picture of the Mott transition. They are also a base to which compare data collected in the antiferromagnetic phase.

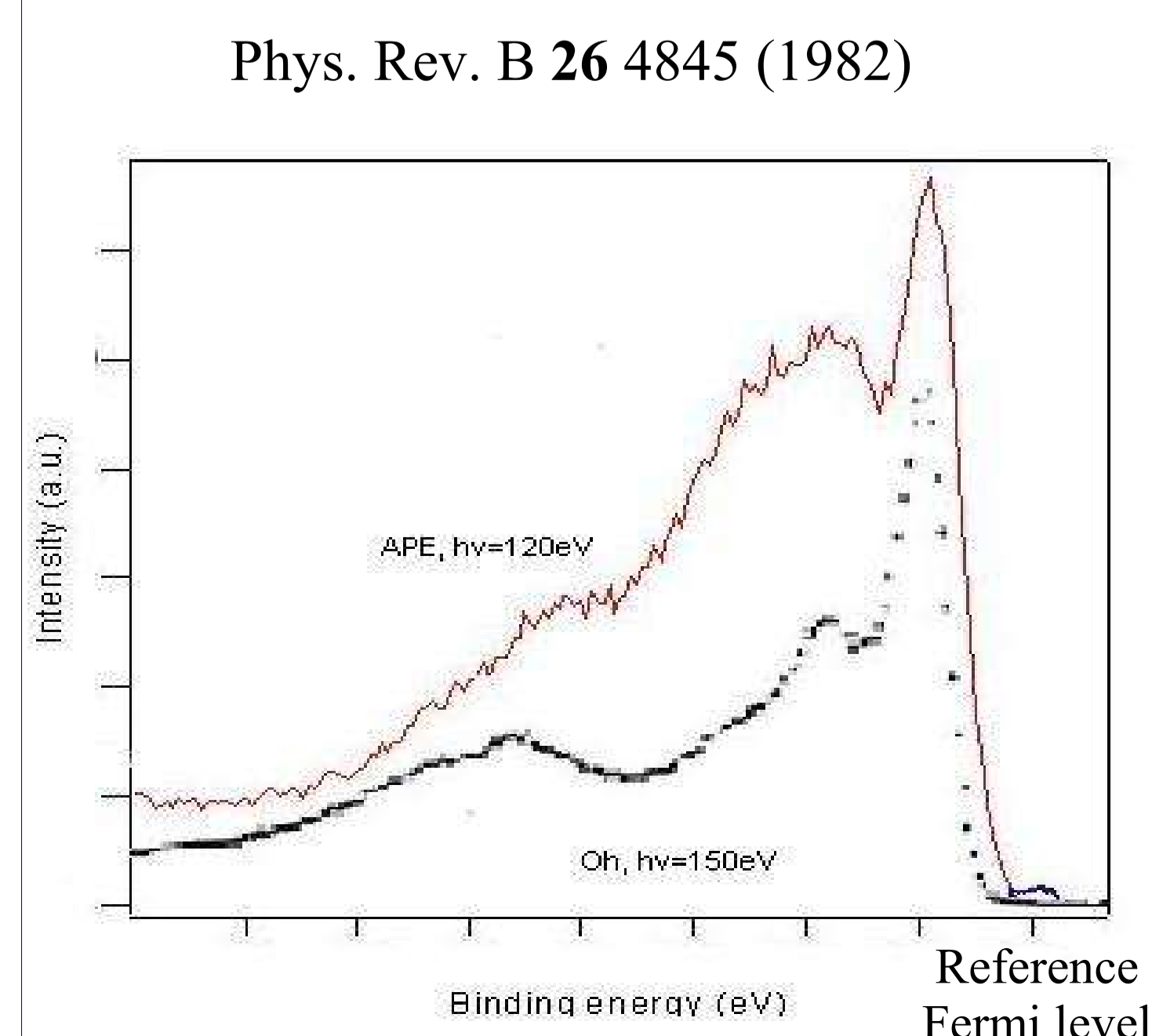
Angle-resolved photoemission spectra



Discussion

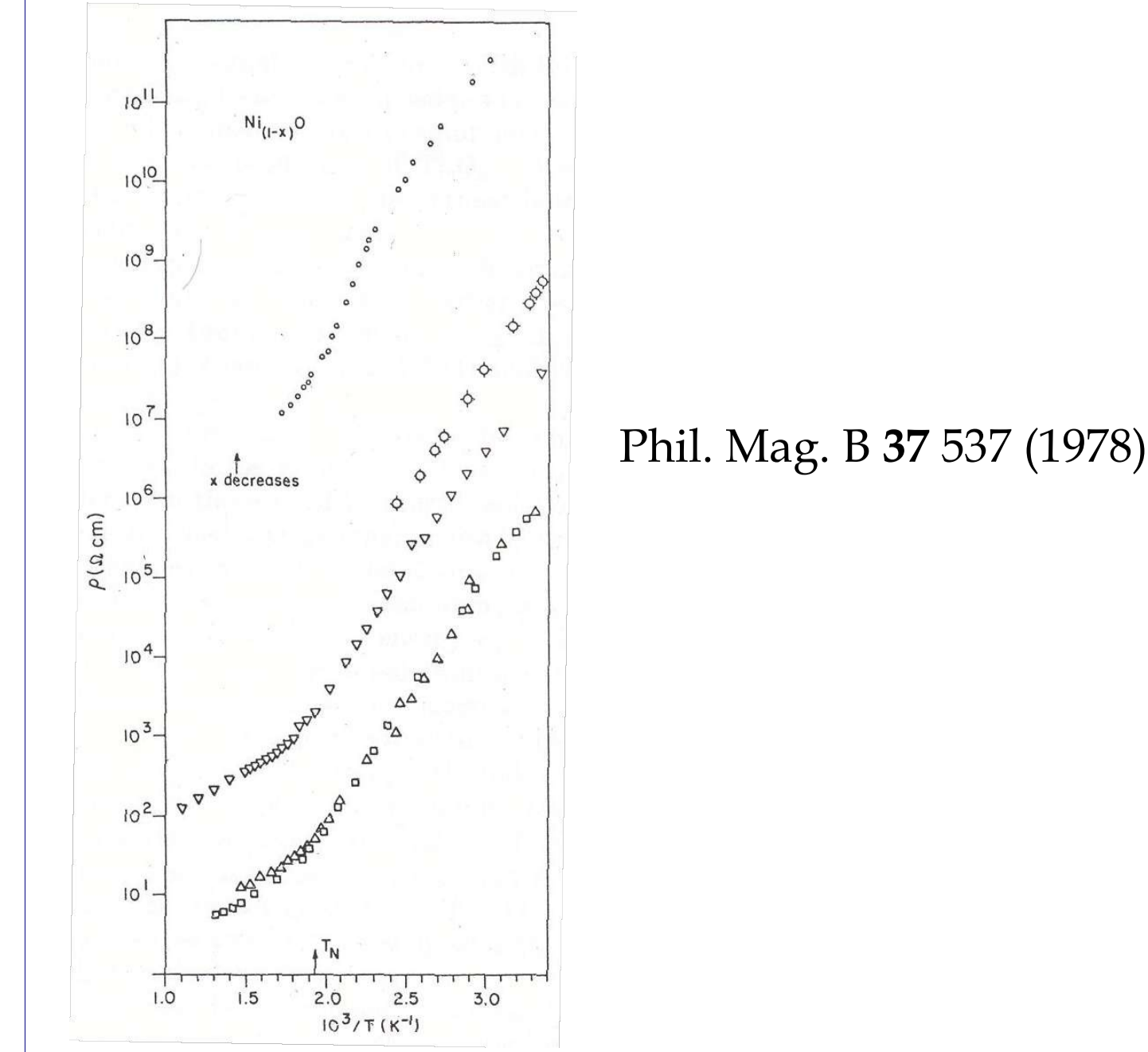
Comparison with other ARPES data

We compared our data with similar angle-integrated spectra taken on a cleaved sample at similar energies. The amount of oxygen is clearly higher in our case (even when rescaled to the cross section energy dependence), while the binding energies and the d^7 and d^8L^{-1} peak intensities are similar.



Transport measurements

A 0.02% stoichiometry variation changes by 10^6 the resistivity. The latter displays no jump at T_N , as for other materials featuring a metal-insulator transition, and no upturn, as for metals. In the whole range NiO behaves like an insulator or a semiconductor. **A gap in the paramagnetic phase is plausible!!**



Theory

Theories which do not include directly the electron-electron correlations (LDA) predict wide bands for NiO. They do not agree with our measurements, in particular at high binding energies.

There are other theories suiting NiO. One of these is the three-body scattering (3BS) formalism (Phys. Rev. Lett. 73 3129 (1994)). It is a kind of configuration-interaction method which includes correlations between configurations containing different numbers of excited photoelectrons and holes in the final state.

This theory predicts very flat bands, as should occur for strongly interacting systems, the right satellite binding energy and a gap of about 4eV at 0K without including the magnetic ordering.

Conclusions & further work

According to our data, the classical picture of Mott transition is not confirmed by our photoemission data. We think this has not been found before for we studied the (111) surface with an alternative preparation method.

The lack of states at the Fermi level implies the Hubbard sub-bands do not join in the "metallic" phase. The conduction is not driven by a change in the electronic structure.

In order to check what stated above we will:

- 1) compare ARPES data with ours;
- 2) compare to 3BS calculated spectra;
- 3) try to measure the value of the gap at various temperatures.