

Valence band studies on transition metal oxides by soft x-ray photoemission

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Beamline BL25SU at the synchrotron facility SPring-8, Japan, has made photoemission spectroscopy of solids feasible also at photon energies in the soft x-ray regime with sufficiently good energy and angle resolution and reasonable signal to noise ratio. At these high energies the bulk sensitivity of the photoemission signal is much enhanced compared to conventional photoemission at low photon energies. This is essential for the investigation of novel bulk properties such as electronic phase transitions. Here we will present results on the Verwey transition in magnetite (Fe_3O_4) and the triplet superconductor/spin density wave system $\text{Sr}_2\text{Ru}_{1-x}\text{Ti}_x\text{O}_4$.

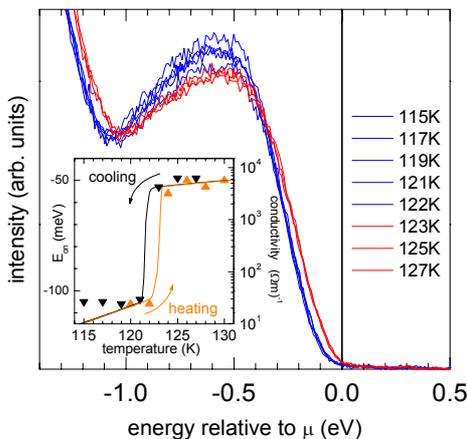


Fig. 1: Near μ spectra of a fractured Fe_3O_4 crystal as a function of temperature. The first order phase transition is clearly visible in the leading edge and compares well to the observed hysteretic behavior in the resistivity (see inset).

Magnetite is a mixed-valent transition metal oxide. It is famous for its quite unique first-order phase transition at $T_V \approx 123\text{K}$, the so called Verwey transition [1]. There the resistivity jumps upon cooling by about two orders of magnitude. Although known for a long time this transition is currently a matter of intensive debate questioning fundamental issues such as the charge ordering of $\text{Fe}^{2+}/\text{Fe}^{3+}$ ions below T_V on the B-sublattice of the inverse spinel structure which is widely

believed to be the driving mechanism. Utilizing the enhanced probing depth of soft x-rays and different surface preparations we were able to deconvolute bulk and surface contributions [2]. It turned out that the Verwey transition is visible only in the spectra of fractured surfaces. It shows up as a discontinuous jump of the leading edge at the bulk transition temperature superimposed on an otherwise gradual temperature dependence (see Fig. 1). Thermally prepared well-ordered surfaces do not show such a discontinuity but only the continuous shift as a function of temperature.

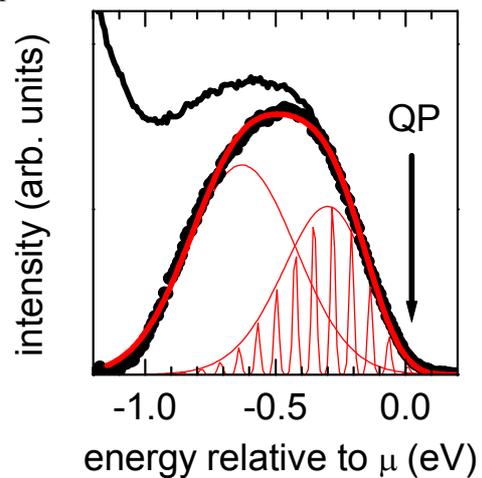


Fig. 2: 180K spectrum of Fe_3O_4 and fit for a polaronic model of the spectral lineshape (red lines).

Another remarkable feature of the observed spectra is that there is no spectral weight at the chemical potential μ let alone a well-defined quasiparticle peak. Other materials, displaying metal-insulator transitions of the Mott type do show such a peak in the metallic phase. Against the background of other recent experimental data on magnetite the near μ spectral lineshape can consistently be explained if one accounts for the apparently strong coupling of the electrons to the lattice. By forming small polarons actually the spectral weight of the near μ quasiparticle peak can be exponentially small and be shifted

to higher binding energies into multiple phononic sidebands. The situation is depicted in Fig. 2. Thus we conclude that the Verwey transition also contains aspects of a cooperative Jahn-Teller effect (note that the Fe^{2+} ions are Jahn-Teller active) besides the importance of interatomic Coulomb energy between the Fe ions on the B-sublattice.

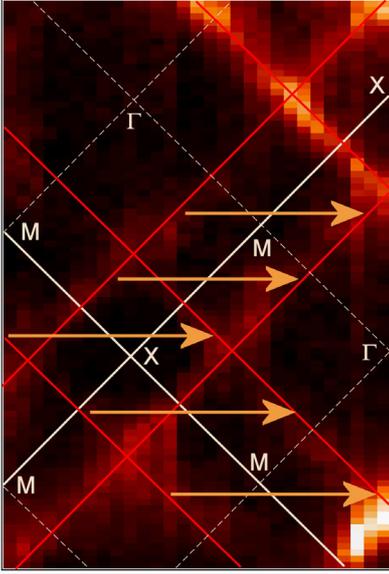


Fig. 3: FS map of $\text{Sr}_2\text{Ru}_{0.91}\text{Ti}_{0.09}\text{O}_4$. For details see text.

Quite recently it was observed that in the triplet superconductor Sr_2RuO_4 substituting the Ru^{4+} ion by the non-magnetic d^0 -ion Ti^{4+} induces local-moment magnetism, which statically orders for $\text{Sr}_2\text{Ru}_{1-x}\text{Ti}_x\text{O}_4$ with $x \gg 0.03$ [3,4]. This behavior was confirmed by elastic neutron scattering which observes the formation of a static incommensurate spin-density wave (SDW) for $x = 0.09$ below $T_{\text{SDW}} = 25$ K [5]. The question arises how the doping and the SDW affects the electronic structure and how the occurrence of the SDW instability may be related to the nesting properties of the Fermi surface (FS).

To elucidate these questions and to circumvent possible effects by the surface reconstruction in these compounds we performed high-energy photoemission measurements to investigate both the bulk Fermi surface topology and possible changes of the electronic structure upon doping.

A Fermi surface map of the doped system is displayed in Fig. 3. Indicated is the hidden quasi-one-dimensional character of the FS (red lines) and the possible nesting by marking the SDW wavevector as obtained from neutron scattering (arrows). In comparison to the

undoped system, surprisingly, the Fermi surface and especially the Fermi surface “volume” remain essentially unchanged indicating that the Ti-ions do not much affect the states close to the Fermi energy.

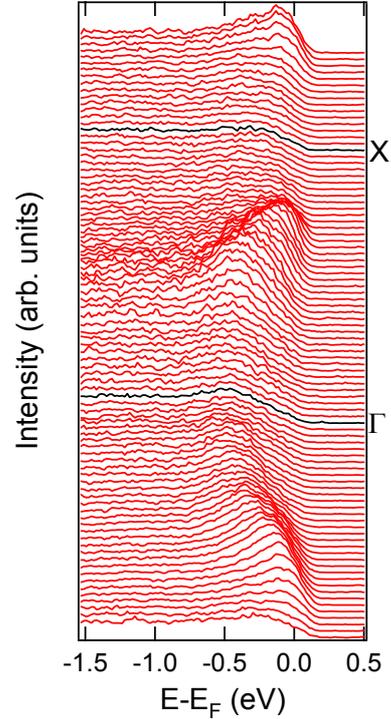


Fig. 4: Angle resolved energy distribution curves along the ΓX high-symmetry line of $\text{Sr}_2\text{Ru}_{0.91}\text{Ti}_{0.09}\text{O}_4$.

If the electronic structure is not much affected at the Fermi energy one would at least expect a relatively large disorder potential to be induced by the Ti ions. This in turn should be reflected by broadened structures and a lack of dispersion especially in the low-lying bands of Ti-doped Sr_2RuO_4 . A typical series of energy distribution curves along a high-symmetry line is shown in Fig. 4. Again it is very surprising to find strong dispersing features comparable to the undoped compound.

In summary, our observation points to the fact that the Ti 3d states do not participate in the formation of the conduction bands but are rather shifted to energies far away the chemical potential. Only a moderate disorder potential is induced by the Ti ions.

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