



Half-metallic Ferromagnets and Spintronics

Transition-metal oxides exhibit anomalous and interesting physical properties. Those properties are determined by the coupling between charge, orbital and spin of valence electrons. They can be tuned by controlling the composition, temperature or other physical variables. Synthetic thin films of transition-metal oxides therefore offer new opportunities both for fundamental research and technological applications such as spintronics. For instance, magnetic oxides have drawn much attention because of colossal magnetoresistance and half-metallic behaviour.

Half-metallic magnets, in which one spin channel is conductive but the other one is insulating, are important potential materials for spintronics. To be a half-metallic magnet, the material has a partially occupied band for one spin direction whereas for the other spin direction it has a fully filled band separated from the unoccupied band by a bandgap. The uppermost occupied energy level of the partially filled band defines the Fermi level, which lies within the bandgap of opposite spin. Perfect spin polarization of conduction electrons is potentially useful. The emerging science of spintronics seeks to exploit the two separate spin channels in electronic devices in which half-metallic electrodes act as sources of spin-polarized electrons and as magnetically-controllable spin filters.

One of the basic components in spintronics is a spin valve structure composed of a magnetic sandwich grown on an antiferromagnetic substrate. The magnetic sandwich structure consists of two magnetic layers separated by a non-magnetic spacer; its magnetoresistance strongly depends on the relative orientation of two

ferromagnetic layers separated by a nonmagnetic layer, as shown in Fig. 1. As a consequence of spin dependent scattering, parallel alignment of magnetizations in the magnetic layers leads to a decrease in resistance. The directions of the magnetic moments can be manipulated by external magnetic fields applied to the spin valve. If we use half-metallic materials as the magnetic layers in a spin valve, the magnetoresistance will be greatly enhanced because conduction electrons exhibit spin-polarization of 100%. In such a spin valve, the only states available to the conducting carriers are those for which the spins of the carriers are parallel to the spins of the half-metallic magnets. The spin valve can function as a conductor or an insulator, depending on the alignment of the magnetizations in the magnetic layers. Any change of external magnetic field thus will result in a dramatic change in resistance, i.e., magnetoresistance. Devices such as spin valves

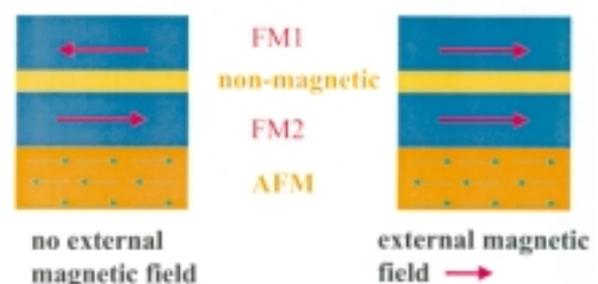


Fig. 1: Cross-section view of a spin valve structure consisting of a magnetic trilayer grown on a antiferromagnetic substrate. Left panel: The magnetic moments of the two ferromagnetic layers are anti-parallel aligned if there is no external magnetic field. Right panel: In the presence of an external magnetic field, the magnetic moments of the two ferromagnetic layers are parallel aligned.

based on the spin of carriers can have numerous applications in information storage.

Measurement of the spin polarization of conduction electrons is essential to unravel the electronic structure associated with the half-metallic feature of transition-metal oxides. The methods available are spin-resolved photoemission and inverse photoemission, spin-resolved soft X-ray absorption, and transport measurements in point contacts and tunnel junctions, either with two ferromagnetic electrodes, or with one ferromagnetic and one superconducting electrode. Synchrotron-based spectroscopic measurements such as photoemission and soft x-ray absorption spectroscopies are key experimental tools in understanding the origin of the unusual physical properties of these materials. Recent advancement in spectrometers, soft X-ray beamline optics and undulator technology has opened up new opportunities for the spectroscopic studies. Advanced techniques of thin film synthesis enable an alternative approach to the manipulation of their magnetic and electrical properties, providing us an avenue for frontier research in strongly correlated systems such as thin films of transition-metal oxides.

With molecular beam epitaxy (MBE) or pulsed laser ablation deposition (PLD) techniques, epitaxial thin films of transition-metal oxides are generally grown on single crystal substrates of metals or oxides. Oxidation of the thin films can be achieved by introducing atomic or molecular oxygen while the transition-metals are evaporated

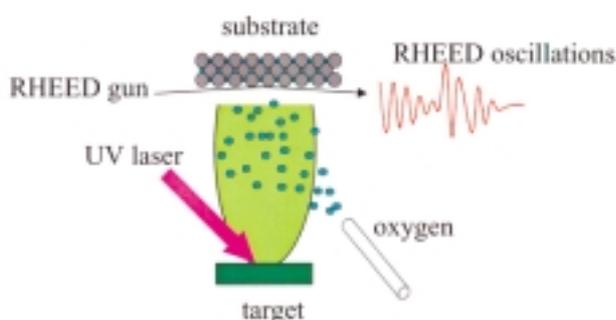


Fig. 2: Schematic diagram of the set-up for epitaxial oxide thin film growth showing two complementary growth methods, MBE and PLD. Oxidation of the thin films is achieved by means of introducing atomic or molecular oxygen while the transition-metals are being evaporated. RHEED is used to monitor the atomic structure of oxide thin films, and the thickness is calibrated by RHEED oscillation.

from a crucible in a MBE cell with thermal heating from a surrounding filament, or ablated from a target by a UV laser, as shown in Fig. 2. To ensure the epitaxy of the films, such systems generally incorporate a reflection high-energy electron diffraction (RHEED) system for real-time monitoring the atomic structure of oxide thin films. These samples provide great opportunities for spectroscopic studies of electronic structure of thin films of transition-metal oxides with well-controlled stoichiometry. Fig. 3(a) and 3(b) show our two complementary MBE and PLD growth systems of oxide thin films, respectively.

We have performed synchrotron-based spectroscopic studies of the simplest half-metallic ferromagnet CrO_2 . First-principle calculations using the local-spin-density approximation (LSDA) elucidate that the majority spin states cross the Fermi level while the minority spin states show a band gap. Point contact measurements at superconductor-metal interfaces reveal a spin-polarization of the conduction electrons larger than 90%, supporting the half-metallic nature predicted by band theory. On the other hand, its magnetic susceptibility in the paramagnetic phase shows a Curie-Weiss like behavior, indicating the presence of $3d_2$ local

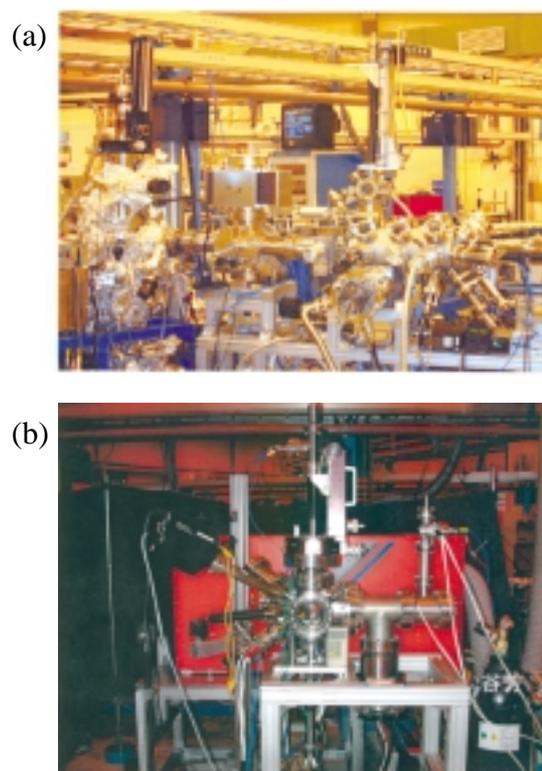


Fig. 3: Photographs of two complementary oxide growth chambers, MBE (a) and PLD (b).



moments, suggesting a mechanism for ferromagnetism beyond the standard band or Stoner-like model. To reconcile these two apparently contradictory findings, it is essential to address two important questions related to the influence of electron correlation effects on the physical properties of CrO_2 . They are: why it is metallic despite the presence of strong electron correlation effects, and why band structure calculations can explain its half-metallic property but fail completely for the electronic structure of many other 3d transition-metal oxides.

Several recent experiments reveal that electron correlations are essential to account for the underlying physics of CrO_2 , including photoemission, soft X-ray absorption (XAS), resistivity, and optical measurements. Self-doping concept has been proposed to explain the anomalous physical properties of CrO_2 based on LSDA+U band structure calculations, which indicate that Coulomb interactions indeed play an important role in the electronic structure. This picture is also proposed in a very recent model that includes orbital correlations. The latest LSDA calculations, however, conclude that there is no need to include strong correlations of the Hubbard type.

In order to determine the electronic structure of CrO_2 and to verify the predictions made by the various spin-dependent band structure calculations, we have used a newly developed spin resolved absorption technique to explore the spin-polarization of the states above and around the Fermi level. O $1s$ XAS spectra in a spin-resolved mode can be obtained with collecting the O KLL Auger partial electron yield using an electron energy analyzer, which is equipped with a micro-Mott spin-detector. We explain the underlying concept of this type of spin-resolved measurement as follows. If the unoccupied O $2p$ partial density of states of magnetic oxides is spin-polarized as a result of charge transfer, so will be the O $1s$ hole in the XAS final state, since the O $1s \rightarrow 2p$ transition conserves spin. The subsequent KLL Auger decay of the XAS state leads to O $2p^4$ like final states, and the outgoing Auger electron will now also be spin-polarized. Unique to a KLL Auger decay is that all two-hole final states are of pure singlet 1S and 1D symmetry because the triplet 3P symmetry

transitions are forbidden. This implies that all the O KLL Auger electrons will have an equally high degree of spin-polarization as the O $1s$ hole and the unoccupied O $2p$ density of states, with, of course, an opposite sign because the transition is singlet in character. We note that this type of spin-resolved O $1s$ XAS is different from a measurement of magnetic circular dichroism (MCD) in O $1s$ X-ray absorption. In the latter the helicity of the circularly-polarized light is varied and the dichroic signal contains more convoluted information about the spin and the orbital moments transferred from the cations.

Fig. 4(a) shows spin-polarized O $1s$ XAS of CrO_2 taken with the \mathbf{E} vector of the light perpendicular to the c -axis of the crystal. The photon energy resolution is set to 0.4 eV. The top

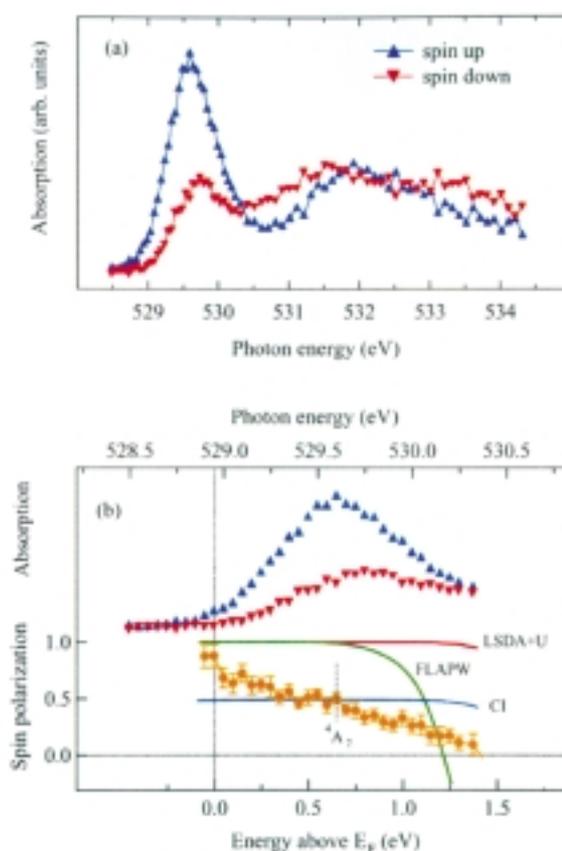


Fig. 4: (a): Spin-resolved O $1s$ absorption spectra of CrO_2 films with $\mathbf{E} \perp c$. Top panel of (b): Spin-resolved O $1s$ absorption spectra in the vicinity of the main peak. Bottom panel of (b): Spin-polarization of O $1s$ spectrum (filled circles), and calculated spin polarization curves obtained by LSDA+U (dotted line), FLAPW (dashed line) and cluster CI (solid line) calculations.

and the bottom panels of Fig.4 (b) present the spin-resolved O 1s XAS spectrum and its spin polarization in the vicinity of the main peak, respectively. The measurement shows that the closest states to the Fermi level have a spin-polarization of $(85 \pm 10)\%$. These states are therefore almost fully spin-polarized, consistent with the predictions of band-structure calculations and the Andreev reflection measurements at the superconductor-metal interfaces. Our spin-resolved results provide direct spectroscopic evidence that CrO_2 is half-metallic. Strikingly, the spin-polarization of the main peak at 529.6 eV is only 50%. This is in strong disagreement with all band structure calculations, which predict that the polarization of this feature of the conduction band should be 100%. In fact, the spin polarization from band-structure calculations show a constant spin polarization of 100% for energies from the Fermi level all the way to (and also beyond) the position of the main peak. This discrepancy can be taken as an indication that strong correlation effects are present in the system. It is typical that the concept of density of states, as defined in effective one-particle theories, loses its meaning as a basis for a quantitative understanding of excitation spectra, i.e., density of states are then considerably different from spectral weights.

It is remarkable that the spin polarization of the states near the Fermi level can be reproduced by band theory, but not by the cluster calculations (CI), while the spin polarization at higher energies can be explained by CI but not by band theory. These spin-resolved data therefore strongly suggest that the electronic structure of CrO_2 is very dualistic in nature, in the sense that the states at the Fermi level are band-like while those at higher energies are localized. In addition, the temperature dependence of the XAS measurements also support that CrO_2 exhibits $3d^2$ local moments, consistent with the conclusion of our spin-resolved measurements and the magnetic susceptibility measurements of CrO_2 , which reveal a clear Curie-Weiss like behavior in the paramagnetic phase.

In conclusion, we have presented synchrotron-based spectroscopic investigations of half-metallic ferromagnets for spintronics. Particularly spin-

resolved spectroscopic studies of half-metallic oxides CrO_2 have been demonstrated. We have also summarized experimental techniques for growth and spectroscopic studies of transition-metal-oxide thin films, which exhibit strong electron-electron correlation effects and important subjects in frontier condensed matter physics. We found that the combination of synthesis techniques of thin film with synchrotron-based spectroscopies yield great opportunities to explore modification of electronic and magnetic properties, orbital magnetism, and novel phase transitions of transition-metal oxides.

Beamline:

05B1 EPU beamline

Experimental Station:

Spin polarized PES end station

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Publications:

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