



DETECTION OF ORBITAL ORDER IN TRANSITION METAL OXIDES BY RESONANT X-RAY SCATTERING

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The transition metal oxides have fascinated chemists and physicists for many decades with their intriguing structural, magnetic and electronic properties. One of the remarkable phenomena displayed by a number of these compounds is the Jahn-Teller effect, in which an orbital degeneracy of the transition metal ion is lifted by a low-symmetry lattice distortion, which «chooses» one of the degenerate states. In a lattice of such ions one can encounter a cooperative

Jahn-Teller effect, in which the occupation of the degenerate orbitals displays long-range order, characterized by a well-defined wavevector. For example in LaMnO_3 , the Mn ions are partitioned in two sublattices, in which the $3d_{(3x^2-r^2)}$ or, respectively, the $3d_{(3y^2-r^2)}$ orbitals are occupied. It turns out that orbital order can be favoured not only by the consideration of lattice distortions, but also by other mechanisms, notably by magnetic interactions. This is because the relative orientation of occupied d orbitals in neighbouring ions determines the strength and sign of the indirect exchange (superexchange) interaction between their spins.

Recently, in view of the high current interest on transition metal oxides stimulated by the discovery of cuprate high-temperature superconductors and of colossal magneto-resistance in the manganates, orbital order phenomena have been paid much attention. One aspect which was discussed during the ESRF workshop on Magnetic Scattering is the possibility of a direct observation of orbital order by resonant x-ray scattering at the K edge of the transition metal. This could give a direct handle to the order parameter of this peculiar kind of ordered state, and a measure of its temperature dependence, and the relationship of its onset to structural or magnetic phase transitions, thus contributing to an understanding of its origin. In fact there is up to date no

satisfactory way to observe and measure the orbital order parameter, although in principle non-resonant diffraction should detect the corresponding change in the shape of the electron density. The corresponding signal is however expected to be weak (less than 0.1 electrons per unit cell).

In some recent theoretical work done at the ESRF by M. Fabrizio, M. Altarelli and M. Benfatto, the idea is to exploit the sensitivity of resonant scattering of polarized x-rays to the availability of empty intermediate states of the appropriate symmetry. In an orbitally-ordered system, they are available on one sublattice but not on the other. In this work the particularly intriguing case of V_2O_3 was considered; in this compound, the wavevector of the orbital order has never been experimentally measured and is not unambiguously determined by theory; recent indirect evidence, is in some cases, interpreted as strongly supporting the existence of orbital order, and in some others as putting the very existence of orbital order in question. The conclusion of the Authors, which has not yet been verified, is that orbital order should be directly observable by resonant scattering and therefore all controversy could be settled by experiments.

In experiments performed by Y. Murakami et al. on $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$ as well as on LaMnO_3 , a signal at the wavevector of the expected orbital order was detected, which was strongly resonant at the dipole edge corresponding to the Mn 1s to 4p transitions. In theoretical work done in Sendai by S. Ishihara and S. Maekawa, the sensitivity to orbital order was ascribed to a modulation of the energy of the empty 4p levels depending on the selective occupation of the 3d orbitals. These results of the Japanese groups were reproduced in Brookhaven by D. Gibbs and M. Blume. In our opinion, more work is called for, in order to verify whether the 4p level energy modulation is controlled by other factors or not, such as the displacement of the ligand oxygens.

In summary, the workshop provided a very timely opportunity to discuss the contribution of x-ray scattering to the investigation of orbital order, bringing together the groups involved in this problem at the ESRF, at NSLS and in Japan. ■

PROBE COHERENCE VOLUMES AND THE INTERPRETATION OF SCATTERING EXPERIMENTS

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One of the significant features of synchrotron radiation, especially that from 3rd generation insertion devices, is the small-energy bandpass of the emitted radiation. In the case of undulator beams monochromatized by Si crystals at the ESRF, the wavelength bandpass ($\Delta\lambda/\lambda$) attains $\sim 10^{-4}$. As a result the photon beam exhibits partial coherence with a longitudinal coherence length $\xi_L = \lambda/(\Delta\lambda/\lambda)$ of the order of $1 \mu\text{m}$ for 1 \AA x-rays. The possibility of coherence over such dimension is fundamental to the experiments involving «speckle» patterns at the ESRF, but it is also an important consideration when conventional scattering experiments are performed, especially when the quantity ξ_L becomes comparable to the dimensions of the material being studied, or with the extinction length; the latter being written as $1/\mu$ and corresponding to the length over which absorption reduces the intensity of the radiation by a factor $1/e$. Within a coherent volume the amplitudes rather than the intensities of the scattering process must be added. We emphasize here that these ideas are independent of the perfection of the crystal scattering the photon beam, i.e. they apply equally to both the kinematic and dynamic theories of diffraction, although the treatment in the two cases is, of course, different.

The standard procedure for correcting for absorption involves correcting the intensities diffracted from a volume of scattering, i.e. the interference between the amplitudes is first calculated to give the beam amplitude for a given reflection, and then the absorption correction is made on the final intensities. This is appropriate when the extinction length

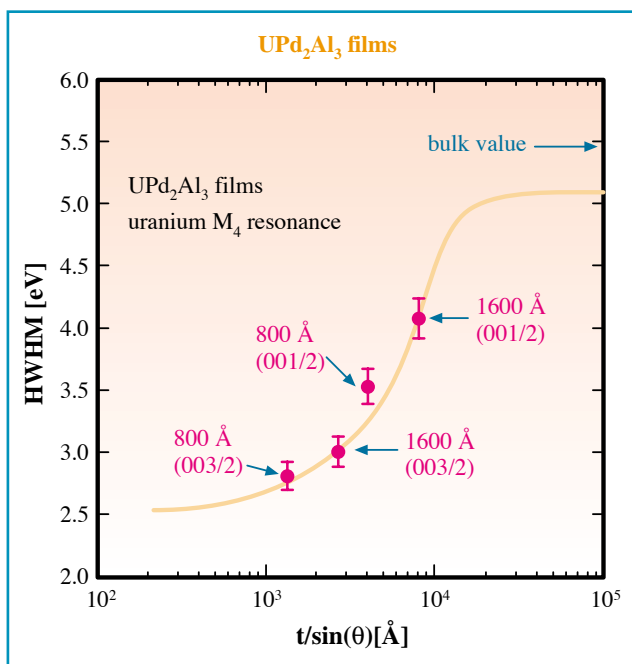


Fig.1: Energy half-width of the antiferromagnetic peaks (all at $T = 4$ K) at the M_4 absorption edge as a function of optical path length ($t =$ film thickness, and θ is the Bragg angle for a reflection) of the photon beam in the thin films of UPd_2Al_3 . The dashed curve is the numerical simulation assuming that the ordering is established throughout the film thickness.

is large and the coherence volume is small, $1/\mu > \xi_L$, such as when a laboratory source is used and the wavelength is far from an absorption edge. However, it is inappropriate when resonant scattering experiments (i.e. the photon energy is tuned to an absorption edge) are performed at a synchrotron source. For example, at the actinide M edges $\mu \sim 20,000 \text{ cm}^{-1}$ so that $1/\mu \sim 0.5 \mu\text{m}$ and clearly $1/\mu < \xi_L$ in this case.

These ideas have been pursued and numerical routines developed to simulate possible situations. Space does not permit a complete description of the theory, but we will illustrate how these ideas influence scattering patterns actually observed on the magnetic diffraction beamline, ID20. Magnetic resonant scattering occurs when the photon beam is tuned to a particular resonance and a large enhancement of the (usually weak) magnetic cross-section occurs. The largest such effects have been found to be associated with actinide M edges, when the enhancement of the magnetic cross-section can reach a factor of $\sim 10^6$. At the same time the absorption is such that the probe becomes essentially one of the near surface region. In this extreme situation, numerical simulations show that the exact form of the scattering, especially its energy dependence, which changes the extinction length, will depend on the spatial localisation of the

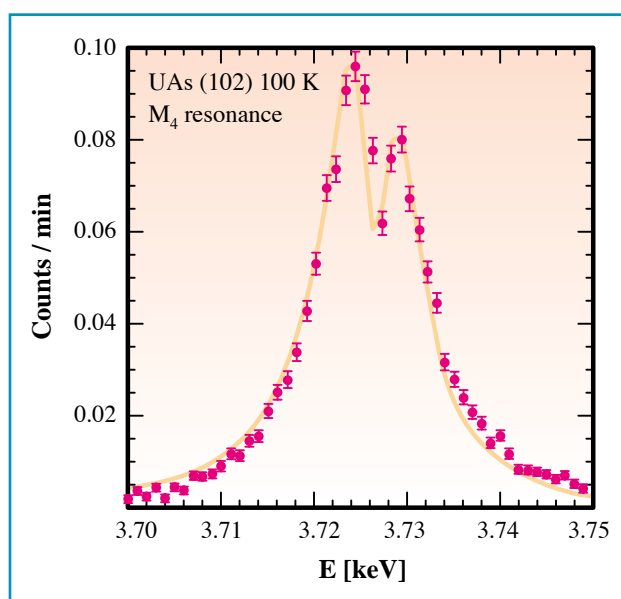
scattering centres. This is a new concept, coupling the spatial aspect within the sample being examined to the energy dependence of the scattering intensity.

The first example is taken from experiments on thin films of the antiferromagnet UPd_2Al_3 . The films have thicknesses (t) 800 and 1600 Å and were grown epitaxially on the (111) surface of $LaAlO_3$ by co-evaporation of the elements. The antiferromagnetic (AF) order of the compound is alternating (001) layers of ferromagnetic spins so that the new Bragg peaks produced by the AF repeat distance are $(0, 0, n/2)$ where $n =$ odd integer. Figure 1 shows the results of measuring the

energy-dependence of the scattered intensities for two different values of n , and for the two films. There is a clear tendency for the narrowest energy widths to be achieved when the photon beam has the shortest optical path in the material. The dashed curve is the result of numerical simulations considering that the probe and sample transverse coherence may be neglected; as shown, the simulations capture the essential behaviour. At $T = 4$ K these films are ordered throughout their thickness, and provide a good test of the theory because of their limited thickness. Just below the ordering temperature T_N only the top part of the films orders magnetically and this may be seen by a 20% narrowing of the energy width of the $(0, 0, 1/2)$ reflection for the 1600 Å film. The best fit to this energy profile suggests that only the top 600 (± 50) Å of the film is magnetically ordered at this temperature. The lack of homogeneity is assumed to arise from the 0.15% interfacial strain between the film and the substrate.

The second example is taken from experiments on another uranium antiferromagnet UAs. The experiments are performed on an infinitely (several mm) thick crystal. In Figure 2, we show the energy profile as a function of photon energy when the crystal is near T_N . The profile clearly shows split peaks. This cannot arise from ordering just at the surface, as was seen above in the films, and which always gives rise to a narrowing of the energy width. Instead in this case there is a non-diffracting layer of some 400 Å at the

Fig. 2: Energy profile of an off-specular antiferromagnetic reflection from UAs taken near T_N on ID20. The solid line is a fit to the data employing the model described in the text and assuming that there exists a non-diffracting layer of 400 Å of the same material on top of the crystal. This belongs to another domain and so diffracts into a different direction.





surface of the UAs crystal that actually corresponds to another magnetically-ordered domain not probed by the off-specular (102) reflection. The solid line is a fit, and it reproduces the data very well.

In conclusion, we have introduced the idea that the «probe coherence volume» plays an important part in the interpretation of diffraction data taken at the ESRF. This represents a re-examination of assumptions conventionally used to interpret diffraction data. In most cases the

probe coherence volumes are small – special efforts have to be made to increase the monochromaticity of the beam, which usually result in an unacceptable loss of intensity. However, these new conditions are encountered with synchrotron sources, especially with the new undulator beams, and care must be taken to understand the consequences. In the presence of strong absorption, new effects arise and we have shown that in certain cases the *energy* dependence of the intensity may be used to identify

the *spatial* localization of the scattering centres. This opens the way for further experiments exploiting the partial coherence of the incident x-ray beam. The coherence of x-ray sources and the narrow bandpass beams that are available from undulators at 3rd generation sources make these effects more qualitatively important than previously thought. Discussions during the workshop made this point clear and further emphasised the new information that can be obtained from experimental results. ■



**THE 17TH GENERAL CONFERENCE OF
THE CONDENSED MATTER DIVISION
OF THE EUROPEAN PHYSICAL SOCIETY**



will be held as a joint meeting with the

**6^e «JOURNÉES DE LA MATIÈRE CONDENSÉE»
OF THE FRENCH PHYSICAL SOCIETY**

**at Grenoble (Univ. Campus)
from 25 to 29 August 1998**

It will comprise *seven plenary lectures* given by the following invited speakers: G. Abstreiter (Si/Ge Nanostructures), M. Bruel (Smart Cut of Si), O. Fischer (Superconductivity), J. Pendry (Quantum Friction), Y. Petroff (Synchrotron Radiation), J. Prost (Biophysics) and R. Scherm (Neutron Scattering).

The last plenary session will be dedicated to the *Hewlett-Packard prize-giving*.

Semi-plenary sessions (50 invited speakers) will also be organised as well as *37 parallel mini-colloquia*, selected after a survey among the physicists.

Junior scientists (PhD students) are warmly encouraged to participate. Grants will be offered to cover most of the accommodation expenses and registration fees.

An exhibition of books and scientific equipment will be held during the conference.

We will particularly welcome any initiative in favour of the employment of students and exchange opportunities for postdocs. A round-table discussion on job opportunities after PhD studies will be organized.

Finally, a word about Grenoble. Besides its outstanding scientific

facilities, it has plenty of attractive aspects you may wish to discover. It contains several major museums and the center of the city is very lively at night. At the end of summer, hiking is very appealing and can be done in an area spread over three main mountain ranges which are all within half-an-hour by car of the city center.

The program of the conference is on the Web at <http://www.polycnrs-gre.fr/eps.html>

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