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Hidden states and new peaks in resonant X-ray emission and resonant photoemission¹

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Abstract

Recent developments in resonant X-ray emission and resonant photoemission are discussed. It will be shown that the scattered X-ray energy and intensity distribution of a resonant X-ray Raman scattering experiment contain the excitation spectrum resulting from a single local spin-flip, a well as dd excitations accompanied by local spin-flip satellites. This phenomenon can be used in experiments to determine the interatomic exchange and superexchange interactions, and more generally the local single magnon density of states. Within resonant photoemission, it will be demonstrated that a 'hidden peak' is present in the Auger spectrum of NiO. Proof for the existence of this peak is found in the analysis of the 2p3s3p and 2p3p3p resonant photoemission spectra. © 1998 Elsevier Science B.V. All rights reserved

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1. Introduction

The basis of the theory of resonant X-ray emission and resonant photoemission is well known: the description of the ground state, intermediate state and final state, plus the use of the second-order optical formula, accurately describes the X-ray absorption edges and all resonance experiments carried out at that edge.

The fundamental problem is the combination of local and itinerant effects. The core holes created interact strongly with the valence electrons, which is a local effect, while the electronic properties of the solid are often best described by itinerant models such as Density Functional Theory. In the case of correlated systems, like transition metals and rare

earths, the local effects dominate the description of core level spectroscopy and a successful local model has been built, including core–valence interactions (multiplets), local electric and magnetic fields (i.e. crystal fields) and the use of a series of configurations (i.e. charge transfer) [1].

Though these general concepts are well known, new experiments contain many surprises. In this paper, I will discuss some of the recent developments of the resonant X-ray emission spectroscopy (XES) and photoemission spectroscopy (PES) experiments. The focus will be on the possibility of seeing 'spin-flip' states in resonant X-ray Raman scattering and the presence of 'hidden peaks' in resonant photoemission.

For clarity, it is noted that the concepts 'resonant X-ray emission', 'resonant X-ray Raman scattering' and 'resonant inelastic X-ray scattering' are used as synonyms, as are 'resonant photoemission' and 'resonant Auger'.

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2. Raman peaks and Auger peaks

A central feature of resonance studies is the presence of both Raman peaks and Auger peaks. Raman peaks have a constant transmitted energy, i.e. a constant binding energy in resonant PES. They relate to a transition from the ground state to the respective final states, via a 'virtual' intermediate state. A direct consequence of the second-order formula is that the intensity of Raman peaks follows a Lorentzian shape, and if no other structures are present they can be observed far below (or above) the resonance. Their visibility will be essentially given by the experimental limitations. Auger peaks have constant kinetic energy. In X-ray emission, one speaks of non-resonant peaks which have constant emitted X-ray energy. Auger peaks are seen only at and above the absorption edge. They are related to the process photoemission plus decay, or to the process X-ray absorption–'relaxation'–decay. The phenomena related to this 'relaxation' are not well known in the solid state, and some new insights will be given in the discussion of the 'hidden peaks'.

3. Spin-flip transitions in magnetic transition metal compounds

In recent years it has become clear that it is possible to use resonant X-ray Raman scattering to view directly the dd excitations and charge transfer excitations [2–5]. It can be shown theoretically that the spin-flip transitions should also be visible in magnetic systems [6]. Spin-flip transitions refer to transitions to a state in which the local spin of a site has been reversed, or in general modified. This state relates to an energy which (in the simplest, local, model) relates to the superexchange energy J times the number of neighbours. The scattered X-ray energy and intensity distribution contains the excitation spectrum resulting from a single local spin-flip, as well as dd excitations accompanied by local spin flip satellites.

Using the example of a crystal field multiplet description of a divalent Ni compound, the resonant X-ray Raman scattering intensity is given by:

$$I(\hbar\omega, \hbar\omega') = \sum_{q', q} F_{q'q} \delta_{E_f - E_0 + \hbar\omega' - \hbar\omega} \quad (1)$$

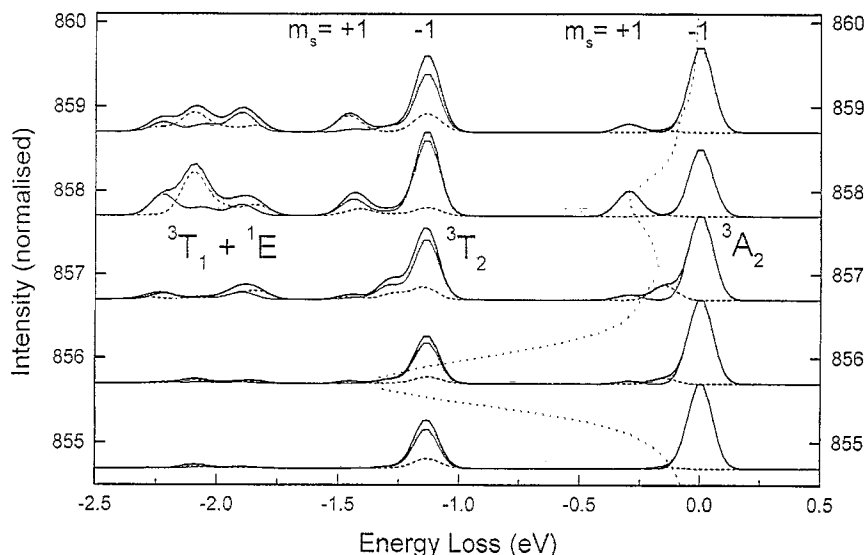


Fig. 1. Resonant X-ray Raman scattering at the L_3 edge of an Ni^{2+} system in octahedral symmetry, using the crystal field parameter of NiO. The F_{xx} scattering (thin solid), F_{xz} scattering (dashed) and the total scattering (thick solid) are given. The X-ray absorption L_3 edge is given with dots and the normalized X-ray Raman spectra are given in steps of 1.0 eV as indicated by their vertical offset. The symmetries of the states are given in the middle spectrum. The m_s sub-states are indicated at the top. Between $m_s = +1$ and $m_s = -1$, the $m_s = 0$ states are visible at the excitation energy of 857 eV.

where the sum extends over the incoming (q) and emitted (q') polarizations. The scattering is described with the Kramers–Heisenberg formula:

$$F_{q'q} = \sum_{3d} \left| \sum_{2p} \frac{\langle 3d^8 | C_{q'}^{(1)} | 2p^5 3d^9 \rangle \langle 2p^5 3d^9 | C_1^{(1)} | 3d_0^8 \rangle}{E_{3d_0^8} + \hbar\omega - E_{3p} - i\Gamma_{2p}} \right|^2 \quad (2)$$

The dipole matrix elements (C_q) to the $2p^5 3d^9$ intermediate states are calculated for all polarizations. The core hole lifetime broadening (Γ_{2p}) does not influence the resolution or line width because of the coherence of the process. The spectrum is broadened by the lifetime broadening of the excited $3d^8$ final states, the dd excitations. The life time of the spin-flipped final states will be given by the spin lattice relaxation time, and the spectral shape and width will display the magnon density of states.

Crucial for the spin-flip transition is the spin-orbit coupling of the intermediate state. Using single particle language, an atomic Y_{22} spin-down state can be excited to the $|3/2, 1/2\rangle$ intermediate state, which in turn can decay to a Y_{21} spin-up state. The overall transition has $\Delta m_s = +1$ and $\Delta m_l = -1$. In a magnetic solid, the spin-up and spin-down states have different energies; for example, the 3A_2 ground state in NiO has a ground state with $m_s = -1$, a state with $m_s = 0$ at about 150 meV and a state at 300 meV with $m_s = +1$. Fig. 1 shows the resonant X-ray Raman scattering at

different excitation energies within the L_3 edge (indicated on the left). An important factor in this scattering process is the angular dependence, as given in Eq. (1). Pure elastic scattering is only possible with F_{zx} , a single spin-flip is possible with F_{xx} and a double spin-flip is again possible with F_{zx} , where z is the scattering in the direction along the magnetization axis and x is perpendicular to it. If the spin-flip transitions are accompanied by dd excitations, more complex situations arise. The experimental study of these spin-flip transitions presents a method of determining the interatomic exchange and superexchange interactions, and more generally the local single magnon density of states.

4. A hidden peak in 2p3p3p resonant Auger spectroscopy of NiO

The discussion of resonant photoemission in transition metal systems (Ni, NiO, CuO) is a lively one [7–13]. A major point of discussion is the ratio between Raman and Auger peaks as a function of energy. In a recent detailed experiment, Finazzi et al. [14] focus on the 3s3s, 3s3p and 3p3p final states at the 2p resonance. These final states cannot be reached by direct photoemission, which simplifies their discussion.

At resonance, the Raman peak of the 3p3p final state can be described as $3d^8 \rightarrow 2p^5 3d^9 \Rightarrow 3p^4 3d^9 + \varepsilon_R$, where the energy of the Raman electron is the difference between the excitation energy and the

Table 1

$\Delta = 3.5$ eV, $U = 7$ eV, $Q = 8.5$ eV: the emitted electrons are respectively the photoemission electron (ε_P), the Auger electron (ε_A) and the Raman electron (ε_R)

Ground state	$3d^8$	$3d^9L$	$3d^{10}LL'$
%	0.811	0.184	0.005
	0	$\Delta = 3.5$	$2\Delta + U = 14$
Inter. state	$2p^5 3d^8 \varepsilon_P$	$2p^5 3d^9 L \varepsilon_P$	$2p^5 3d^{10} LL' \varepsilon_P$
PES	0	$\Delta - Q = -5$	$2\Delta + U - 2Q = -3$
Final state	$3p^4 3d^8 \varepsilon_P \varepsilon_A$	$3p^4 3d^9 L \varepsilon_P \varepsilon_A$	$3p^4 3d^{10} LL' \varepsilon_P \varepsilon_A$
Auger	0	$\Delta - 2Q = -13.5$	$2\Delta + U - 4Q = -20$
Inter. state	$2p^5 3d^9$	$2p^5 3d^{10}L$	—
XAS	$\Delta - Q = -5$	$2\Delta + U - 2Q = -3$	—
Final state	$3p^4 3d^9 \varepsilon_R$	$3p^4 3d^{10} L \varepsilon_R$	—
Raman	$\Delta - 2Q = -13.5$	$2\Delta + U - 4Q = -20$	—

energy of the $3p^43d^9$ state. Above resonance, it is possible to excite a 2p electron by photoemission as $3d^8 \rightarrow 2p^53d^8 + \varepsilon_P \Rightarrow 3p^43d^8 + \varepsilon_A + \varepsilon_P$, where the energy of the photoelectron is given by the excitation energy minus the 2p 'binding energy'. The energy of the Auger electron is given by the binding energy difference between $2p^53d^8$ and $3p^43d^8$.

It is well known that charge transfer effects are important in ionizing experiments. Table 1 includes the charge transfer states $3d^9L$ and $3d^{10}LL'$, plus all related intermediate and final states. An important distinction between PES and X-ray absorption spectroscopy (XAS) is that in the latter the 2p electron has a dipole transition into the 3d band. The relative energy separations due to charge transfer (and also due to multiplets) is the same for PES and XAS, but the relative weight of the charge transfer states is different. In XAS, 80% goes into $3d^9$ and 20% into $3d^{10}$, while in PES 80% goes into $3d^8$, 20% into $3d^9$ and less than 1% into $3d^{10}$. (Noting that the actual states are linear combinations and that there is interference.)

Thus, the $3d^{10}$ state is part of the PES intermediate state, but has no weight, implying that its related Auger final state also has no weight! As can be seen from Table 1, it is actually this state which has the lowest energy in the final state due to the two 3p holes, hence an energy contribution of $-4Q$. Why is this important?

It turns out to be the case that in experiments the Raman peaks are nicely visible before the edge, but immediately at/after the edge the Auger peaks gain intensity. This indicates that there is some relaxation process going on, changing the XAS intermediate state into a relaxed state. An unknown factor is the nature of the relaxation process, and just above the edge the system must find a mechanism to lose its energy, for example by exciting a phonon, a magnon, a dd transition, etc. A potential experimental problem is related to the poor resolution of the X-ray monochromator. If, for example, a single resonance exists with a lifetime broadening of 0.2 eV and a range of 1 eV in energies reaches the sample, then as long as the resonance energy is within this 1 eV, it will dominate. If the peak intensity is then plotted as a function of the mean excitation energy, this creates a peak with apparent constant kinetic energy [7–11]. This implies that it is advisable to use an X-ray resolution better

than the lifetime broadening, say 0.2 eV for 2p core states.

Excitations to the charge transfer satellite at about 5 eV above the edge reach intermediate states dominated by $2p^53d^{10}L$. The relaxed intermediate state contains $2p^53d^{10}$ character, which can decay to the $3p^43d^{10}$ final state at -20 eV. Because, at resonance, one follows the XAS dipole transition, the intensity reaching this final state is much larger than off-resonance (cf. Table 1). Thus, the state which was hidden in off-resonance Auger becomes visible in on-resonance Auger. This is exactly what is observed experimentally: a state at about 4 eV lower energy as the lowest peak of the off-resonance 3p3p and 3s3p Auger spectrum is visible while exciting into the $2p^53d^{10}L$ satellite and disappears at off-resonance energies.

Some more interesting phenomena are observed in NiO. For example, the L_2 Auger peak is not seen in NiO (in contrast to Ni metal [13]). The experimental results, including detailed fits to the spectral shapes, will be published in Ref. [14]. The additional use of Spin-Polarized Circular Dichroism effects is discussed by Nick Brookes in this issue [15,16].

5. Concluding remarks

5.1. Resonant XES

The spin-flip-related peaks should be visible in the resonant X-ray Raman spectrum. This can be used experimentally as a method to determine the interatomic exchange and superexchange interactions, and more generally the local single magnon density of states.

5.2. Resonant PES

Analysis of the position of the peaks in the 2p3p3p and 2p3s3p resonant PES spectra has revealed the presence of an extra peak in the Auger spectrum. This extra peak is 'hidden' in the off-resonance Auger because it does not gain intensity.

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