RESONANT 3s PHOTOESSION AND RESONANT 2p3p3p AUGER OF CaF₂

F.M.F. de Groot*

LURE, Université Paris-Sud, Bâtiment 209D, 91405 Orsay, France

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A theoretical description is given of the 3s resonant photoemission and the 2p3p3p (=L₂₃M₂₃M₂₃) resonant Auger channels in CaF₂. The importance of quantitative analysis is demonstrated and it is shown that the 2p3p3p Auger spectra excited at the 2p X-ray absorption edge do show a large variation if one scans through the edge and excites the different possible symmetry states. These variations are observed in a recent resonant Auger experiment (Phys. Rev. B47, 11736 (1993)); the experiment is reproduced in detail. The analysis shows that the Auger spectra of CaF₂ are completely dominated by the resonance channel, with little contribution of the "normal" Auger channel reached via Coster-Kronig relaxation of the 2p core hole.

Keywords: E. photoelectron spectroscopies, E. X-ray spectroscopies.

1. INTRODUCTION

RESONANT photoemission and resonant Auger spectroscopy at the 2p core levels of transition metals has become an important technique to study the electronic structure of strongly correlated and medium-correlated electronic systems. Recently 2p resonances were used to study CaF₂, CaCl₂ and Sc₂O₃ [1, 2], CuO [3, 4], Ni [4, 5], Co and Fe [6] and a series of 3d oxides [7]. The mechanism to explain the resonances is well known, at least at a qualitative level. Resonant photoemission takes place because the direct photoemission dipole transition interferes with the resonant channel via the deeper core state. This interference effect has been confirmed in numerous studies performed at the 3p edge [8]. 2p3p3p resonant Auger does not show interference. Its intensity is given directly by the 2p X-ray absorption cross section (see below). CaF₂ is an ionic compound with a band gap of 12.1 eV, separating the filled F2p band and the empty CaF₂ can be described in detail with the crystal field multiplet model [9]. In this model the ground state is described in the ionic limit Ca²⁺, represented as 3d⁰.

A few detailed theoretical studies of 2p resonance effects have been published [10, 11]. Van der Laan and coworkers [10] described the detailed 3s, 3p, and 3d resonant photoemission shapes in Ni. For Ni it is crucial to use the Anderson impurity model in order to describe both the 3dⁿ intra-configurational correlations (multiplets) and the 3dⁿ⁻¹,3dⁿ+¹ inter-configurational correlations (charge transfer). Tanaka and Jo [11] describe the 3s, 3p, and 3d resonant photoemission shapes of 3d oxides. They also use the Anderson impurity, or charge transfer, model.

Okada and Kotani showed that for a correct calculation of the satellites in the 2p X-ray absorption spectrum of the 3d⁰-system TiO₂ it is necessary to include charge transfer effects and to describe the ground state as 3d⁰ + 3d¹L [12]. For their calculations of the 3s, 3p, and 3d resonant photoemission of TiO₂ Tanaka and Jo include a similar ground state description. The inclusion of charge transfer is important if the two configurations cross in energy, as is the case for all photoemission experiments, in contrast to X-ray absorption experiments [13]. From the spectral shapes off- as well as on-resonance of 3p and 3d photoemission it is directly visible that the inclusion of charge transfer is crucial [11, 14]. For 3s photoemission and the 2p3p3p Auger decay charge transfer also affects the spectral shape but
2. CALCULATIONS

Figure 1 sketches the dipole transitions (D) and Coulomb matrices (C) for 3s resonant photoemission and the 2p3p3p resonant Auger at the Ca 2p edge in CaF₂. The photoemission to the 3s̄1ε₂ state is indicated with DP. The 2p X-ray absorption process to the 2p53d₁ states has dipole strength \( D_A \). The 2p53d₁ states decay to the 3s-photoemission state via the \( \langle 3s3d; 2p_e \rangle \) Coulomb matrix element \( (C_p) \). The \( D_A: C_p \) and \( D_p \) channels interfere as both reach the identical 3s₁ε₂ final state. The resonance is given by the Fano lineshape and the detailed shape of the resonance is determined by the relative strengths of both channels. The 2p3p3p resonant Auger channel is described similarly: the 2p53d₁ states decay via the strong \( \langle 3p3p; 2p_e \rangle \) Coulomb matrix element \( (C_A) \) to reach the 3p₄3d₁ε₂ final states. These states can not be reached by a direct dipole transition and their total intensity follows exactly the X-ray absorption spectral shape. A small complication is the existence of a strong Coulomb interaction \( (C_f) \) between 3s₁ and 3p₄3d₁ which couples the 3s photoemission and 2p3p3p Auger channels [10, 15]. A range of other Auger transitions can occur from the 2p₅3d₁ states, leading to all two-hole combinations of 3s, 3p and 3d. Also the 2p₅3d₁ states at the \( L_2 \) edge are known to decay via a Coster–Kronig \( \langle 3d_e; 3d_e \rangle \) Coulomb matrix element, leaving the system with a lower energy 2p₃d₁ exciton and an electron–hole pair (e⁺e⁻). With its 12.1 eV band gap compared to the only 4 eV spread of the 2p₅3d₁ excitons these transitions should be impossible for CaF₂. This marks the large difference between insulators and metals (or

| Table 1. Dipole strengths in a.u. Rₙ matrix element in a.u. eV₁/₂. All other parameters in eV, R₁ denotes the direct interaction; R₂ denotes the exchange. The Slater integrals of the 3p₄3d₁ configuration have been scaled to 50% of the atomic values. |
|---------------------------------|-----------------|-----------------|
| Config                        | 2p₅3d₁          | 3s₁             | 3p₄3d₁          |
| \( \langle pp; pp \rangle \)   |                 |                 | R² = 8.32       |
| Spin–orbit                    | \( \zeta_p = 2.40 \) | \( \zeta_p = 0.25 \) |                 |
|                               | \( \zeta_d = 0.01 \) | \( \zeta_d = 0.01 \) |                 |
| \( \langle pd; pd \rangle \)  | F² = 3.04       |                 | F² = 4.80       |
|                               | G¹ = 2.01       |                 | G¹ = 6.40       |
|                               | G³ = 1.14       |                 | G³ = 3.20       |
| CFS                           | 10Dq = -0.9     |                 | 10Dq = -0.9     |
| 2p₅3d₁ →                     | R₁ = -0.00059   |                 | R₀ = 0.064      |
|                               | (C_p) R₂ = 0.039 |                 | (C_A) R² = 0.038 |
| 3s₁ →                        | -0.246          |                 | C₁ = 12.145     |
| 3d₀ →                        | -0.00208        |                 |                 |
|                               | (D_A)           |                 |                 |
|                               | (D_p)           |                 |                 |
semiconductors) for which the electron–hole pairs can be formed and delocalize leaving the system in a relaxed, ionized state $2p^5[3d^1]$. This state can again decay via the $C_A$ Auger decay to a $3p^53d^1\epsilon_p$ final state, which identifies with “normal Auger” in the sense that it occurs at constant binding energy. Because the excited electron of the Coster–Kronig transition delocalizes the $2p^5[3d^1]$ is given under 1+ in Fig. 1. The $2p3p3p$ Auger decay leaves the system in a 2+ state. As discussed this $C_{CK}$ channel is likely to be zero (or very small) for CaF$_2$ (see discussion).

The complete diagram [16] for the 3s resonant photoemission and 2p3p3p resonant Auger is given in Fig. 1. Apart from the inter-configurational Coulomb interactions also a number of strong intra-configurational Coulomb interactions exist, normailly identifed as “multiple effects”. Important are the $(2p3d;2p3d)$ Coulomb (and exchange) matrix elements of the $2p^53d^1$ intermediate state and the $(3p3p;3p3p)$ and $(3p3d;3p3d)$ matrix elements determining the different symmetries within the $3p^53d^1$ Auger final state.

The dipole and Coulomb interaction strengths are calculated with an atomic Hartree–Fock-based programme [17]. They are together with the other atomic parameters and the empirically determined effective crystal field strength collected in Table 1. The 2p X-ray absorption spectrum is calculated from all $3d^0 \rightarrow 2p^53d^1$ dipole matrix elements. Figure 2 shows the 2p X-ray absorption spectrum. The $2p^53d^1$ multiplet is centred at zero. As discussed in detail in [9] good agreement with experiment is obtained. The seven possible transitions in Fig. 2 are broadened with the Lorentzian life time broadening ($\Gamma = 0.2$) and a Gaussian experimental broadening ($\sigma = 0.2$). The open circles denote the excitation energies at which the resonance spectra are calculated. These points have been chosen in order to mimic as closely as possible the experimental results from Elango and coworkers [1].

Figure 3 shows a series of resonant 3s photoemission and 2p3p3p resonant Auger spectra taken at the energies indicated in Fig. 2. The main peak of the $L_3$ edge is given at 0.1 eV and the main peak of the $L_3$ edge is given at 3.6 eV. The results will be analysed in close comparison with the experimental results as given in Fig. 4 of [1].

The 2p3p3p resonant Auger spectra shifts with the step-energy of 0.5 eV to higher kinetic energy while scanning through the edge. Note that this behaviour is different from normal Auger which has a constant kinetic energy. The reason is that for reaching the same peak in the Auger spectrum, the Auger process is accompanied by a “relaxation” of the $3d^1$ electron. In other words, whatever the energy of the $2p^53d^1$ intermediate state, the energy of the $3p^53d^1$ final state has a constant binding energy. A remarkable variation is visible in the shape of the resonant Auger spectra. The $\epsilon_1$ and $\epsilon_2$ spectra (related to the small $\epsilon_0$ peaks in
As discussed above we assume that the $C_{CK}$ channel is indeed zero for CaF$_2$. In their charge transfer analysis Tanaka and Jo also do not include this $C_{CK}$ channel for the 3d-oxides [11]. It should be noted though that this approximation does not hold in general: for Ni metal the $C_{CK}$ relaxation of the $L_2$ edge (and also of the states just above the $L_2$ edge) is very important which has been shown in detail [4, 5]. Also for CuO the "normal Auger" is clearly visible for excitations a few eV above the $L_3$ white line [3]. The relative strength of the $C_{CK}$ channel is determined by (1) the band gap and the details of the density of states close to the Fermi level and (2) the difference between the excitation energy and the energy of the completely relaxed 2p-hole. It is this energy which can be used to excite an electron–hole pair. The precise shape of the relaxed-Auger channel need not be exactly equal to the 'normal' Auger shape because the $C_{CK}$ relaxation is symmetry dependent and does not necessarily reach (only) the completely relaxed state. To understand this problem better a quantitative analysis of the $C_{CK}$ relaxation followed by the $C_A$ Auger (cf. Fig. 1) is needed. A major complication for actual calculations is that one must include the details (like $k$-dependence) of the electron–hole formation.

4. CONCLUSIONS

The 3s resonant photoemission and the $2p3p3p$ resonant Auger spectra of CaF$_2$ are calculated. The recent experiments are reproduced using a crystal field multiplet model, indicating the importance of the symmetry dependence of the resonances. The general model (including charge transfer) to interpret resonant photoemission and resonant Auger is well established. Remaining problems are the precise parameter values to be used in the charge transfer model (discussed in [11]), and their eventual variation in ground, intermediate and final states [13]. Another unresolved problem is the quantitative determination of the $C_{CK}$ channel as a function of excitation energy and material.

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REFERENCES

16. In the calculations also the Auger transitions to a photoelectron of $f$ symmetry are included. The parameters are: $(C_F) R_d^f = 0.0304$, $R_f^f = 0.0860$; $(C_d) R_0^f = 0.081$, $R_0 = 0.081$, $R_0^2 = 0$.