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X-ray absorption and emission from different atoms of the same compound: Success and failure of the single-particle picture

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Theoretical x-ray absorption and emission spectra of crystalline $CoSi_2$ and $NiSi_2$ have been computed considering the single-particle matrix elements between one-electron states. The effect of the core hole has been considered. The validity of the proposed models of absorption and emission processes, based on single-particle calculations and the density of state information that can be obtained from the experimental data is investigated. The comparison with the experimental results shows a different behavior for different atoms: a single-particle approach, namely, the final-state rule, describes the process occurring on a Si atom rather well, but no one-electron calculation is able to interpret transitions involving a Co or Ni atom.

In a transition due to x-ray absorption an electron is excited from a filled core level into an unoccupied state, leaving a core hole behind it. In the case of emission the transition occurs between a filled valence level and an unoccupied core level, existing in the initial state of the atom. The switching on (off) of the core hole in the absorption (emission) experiment is a very strong perturbation and the process is intrinsically dynamic, i.e., the correlation function is time dependent.[1] The possibility of describing the complex dynamical process occurring in absorption and emission spectra in terms of transitions between single-particle states of a static Hamiltonian has been investigated for a long time and important results have been obtained. In simple metals, von Barth and Grossmann[2] proved the validity of the final-state (FS) rule: the simple one-particle approach can be used when the transition matrix elements are calculated from wave functions obtained in the potential of the final state of the x-ray process, i.e., with the core hole in absorption and without the core hole in emission. A different approach of the absorption process, based on the Hartree-Fock (HF) approach and on the single-band approximation, has been proposed by Stern and Rehr.[3] According to these authors the correct single-particle states are neither the initial nor the final ones but something in between. Only in the two limits of transition to nearly empty and nearly filled bands do the appropriate single-particle states reduce to the final and initial ones, respectively.

The strong interest in transition-metal silicides,[4] $CoSi_2$ and $NiSi_2$ in particular,[5] has made available many experimental data on the emission[6-9] and absorption[10-12] processes and we are therefore able to perform a careful investigation of the single-particle approaches. In these compounds the valence electrons show both itinerant and localized character, with a nearly filled *d* band centered around 2 eV ($CoSi_2$) and 4 eV (NiS_2) below the Fermi level E_F.[5] It is not clear if the FS rule, proved for simple metals, is still valid in these systems. Furthermore, opposing recipes are provided from the FS rule and HF approach regarding the wave functions to be used for the evaluation of the matrix elements of the absorption transition: (i) the core-hole excited atom eigenstates (FS rule)[2] or (ii) the unperturbed atom wave functions (HF approach for a nearly full band).[3] This opposing view is generated from the complex nature of the electron states in these compounds, which show both free-electron character and a localized nearly filled band. An interesting point arises from the presence of two different atoms, with only one (Ni or Co) having a predominantly localized character in the valence wave function. Since x-ray emission and absorption are local processes, it is possible to test single-particle theories for processes localized on different atoms. We will show that this is of fundamental importance: only for emission and absorption processes localized on the Si atoms does a single-particle theory, the FS rule, agree with the experimental data, while clearly evident discrepancies, due to dynamical distortions of the spectrum, are found in both absorption and emission spectra localized on the metallic atom.

To investigate the emission and absorption processes we carried out self-consistent calculations of the electronic properties of crystalline $CoSi_2$ and $NiSi_2$. The one-electron energies and wave functions have been computed by the linear-muffin-tin-orbital method in the atomic-spheres approximation.[13] Exchange and correlation contributions to the potential energy have been included though the density-functional description in the local-density approximation.[14] Core electron energies and wave functions were evaluated from the potential energy in the solid, at every step of the iterative self-consistent procedure.[15] From the core and valence state wave functions the single-particle matrix elements are evaluated and parameter-free theoretical spectra are obtained.[16] Two classes of calculations have been performed. The first class involves standard band structure, i.e., ground-state, calculations. The resulting band structures fully agree with the published results.[5] The second class of calculations was necessary in order to correctly describe the excited state due to the presence of a core hole, i.e., the final (initial) state in absorption (emission). The excited atom (an atom with an inner-shell core hole) is formally treated as an impurity. The impurity problem has been self-consistently solved with a supercell technique.[10] The neutrality of the supercell has been assured by adding the extracted core electron to the valence states. The supercell used contains 18 $CoSi_2$ or $NiSi_2$ groups (36 Si plus 18 metal atoms).

One of the requirements determining the (large) dimension of the supercell is associated with the correct description of the screening charge related to the attractive potential of the core hole. A supercell of smaller dimensions, obtained by doubling the lattice constant of the compound a along the three crystal axes, and containing $2^3=8$ groups per supercell, produces a well-defined satellite below the bottom of the valence states. This smaller supercell defines a lattice with a hole-hole nearest-neighbor distance of $1.41a$. A natural way to create a larger supercell would be to treble the lattice constant a, which gives a supercell with $3^3=27$ groups per supercell and a hole-hole nearest-neighbor distance of $1.87a$. Since this last choice cannot be presently performed, by limitation of our computer resources, we obtained an intermediate supercell with 18 groups per supercell and a hole-hole nearest-neighbor distance of $1.58a$. The translational vectors are no longer orthogonal, but form a triclinic lattice. When this intermediate supercell is used, the satellite, which corresponds to the screening electron being localized near the core hole, is merged into the continuum of the valence band. Details of the calculations and of the convergence tests will be published elsewhere.[17] The computed spectra were convoluted with a Lorentz distribution in order to account for the core and valence states lifetimes.[10] No instrumental effect has been included.

We computed the single-particle emission and absorption spectra of crystalline $CoSi_2$ and $NiSi_2$ for the main transitions. Some of our results are shown in Figs. 1 and 2 for emission and absorption, respectively. The experimental spectra[8–11] that we have selected and shown for comparison in Figs. 1 and 2 have been published with the energies referred to the threshold energy (vertical line), usually obtained by x-ray photoelectron measurement of the core-level binding energy.[1] Therefore, we can perform a direct comparison not only for the shape of the lines, as is usually done,[18] but also for the energies. Since the measured intensities are given in arbitrary units, the comparison of the intensities is significant only between the computed spectra, shown with the same units.

The emission spectra (Fig. 1) provide information on the filled part of the valence states. The ground-state results (full line) are given by the site and angular momentum projected density of states (PDOS), modulated by the matrix element effect. The upper, central, and lower panels are determined by the Si p, Si s-d, and Ni s-d PDOS, respectively. The main effect of the presence of the core hole (dashed line) is to shift the valence states towards the bottom of the band (to the left in the figures).[10,19] The first two panels in Fig. 1, relating to transitions involving a Si atom, show an excellent agreement between the single-particle calculations based on the FS rule and the experimental results. This agreement is parameter free and supports the procedure of referring the measured energies to the threshold through the binding energy of the core level, measured from x-ray photoemission. Since a detailed analysis of our results will be presented elsewhere,[17] we emphasize our most striking result shown in Fig. 1 and confirmed by all the transitions investigated: while a single-particle calculation, that suggested by the FS rule, provides a very good description for the Si emission spectra, a definite disagreement between theoretical calculations and experiments is found for the transitions involving metallic atoms. The main feature of the measured Ni M_3 spectrum is shifted by 1.2 eV (3.8 eV) with respect to the computed spectra based on the ground-state (core-hole excited atom) calculation. The extent of the shift is such that it cannot be explained in terms of uncertainties of the computed or measured spectra. An example of such an uncertainty is found in the $NiSi_2$ Si L_3 spectrum (central panel of Fig. 1), where

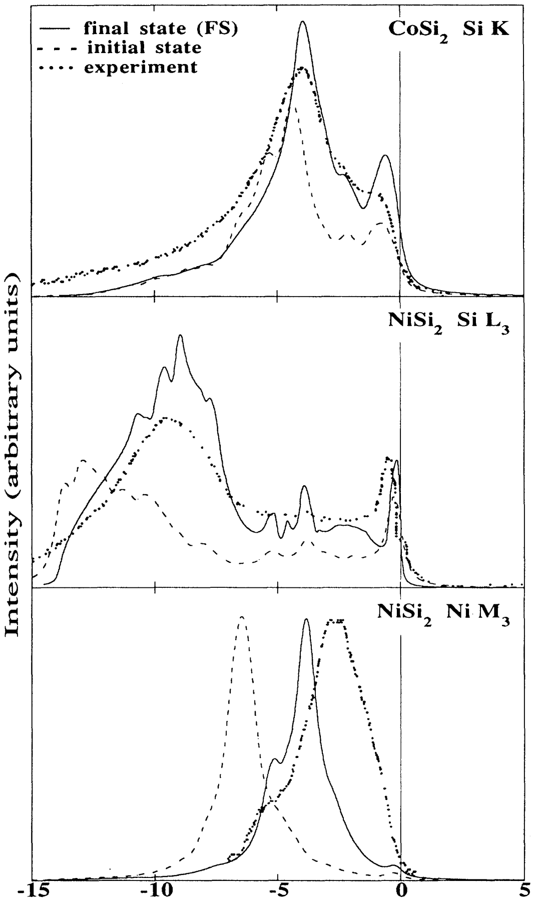

FIG. 1. Comparison between the experimental (dotted curve) and theoretical x-ray emission spectra. Full lines show the results according to the final-state rule (ground-state calculation), while dashed lines refer to the case of the core-hole excited atom. Upper panel: $CoSi_2$ Si K emission (experimental data from Ref. 9); central panel: $NiSi_2$ Si L_3 emission (experimental data from Ref. 8); lower panel: $NiSi_2$ Ni M_3 emission (experimental data from Ref. 8). Energies (in eV) are referred to the threshold E_F (vertical line).

the feature just below the threshold differs by ~0.3 eV in the measured and final- and initial-state spectra. A possible cause of the disagreement between measured and computed Ni M_3 spectra may be due to the alignment procedure of the spectra, if the screening energy of the core hole is different in the x-ray emission and x-ray photoemission spectroscopies. It can be easily checked that this effect cannot explain the disagreement. In the emission experiment the core hole is fully screened and a difference may be only due to a partial screening of the core hole in the photoemission experiment. In this case the photoemission binding energy would not produce a correct alignment, but the emission spectra would result at lower energies. Therefore, it would be necessary to correct the procedure by shifting the emission data at greater energies, increasing in this way the disagreement with the Ni M_3 computed spectrum (Fig. 1).

Actually the disagreement is basically due to the different shape of the high-energy part (to the right in the figure) of the theoretical spectrum, with a long tail in both the computed spectra absent in the measured one. Note that all spectra present the same (small) peak at the threshold. Since we considered all single-particle effects, and since any intermediate single-particle spectrum will lie between the two shown in Fig. 1, our result proves the failure of the single-particle picture to describe the emission process from atoms with localized electrons, like Ni or Co. The energy location of the *d* band of Ni or Co as measured from an x-ray emission experiment is therefore different from that of the ground-state PDOS. This behavior is opposite to that of Si atoms in the same system, where final-state rule is well observed.

Similar conclusions hold also for the absorption transitions (Fig. 2), not only for the emission ones. Note that the computed curves do not include any instrumental broadening. Nevertheless it is evident that only for transitions involving the Si atoms can a single-particle calculation interpret the experimental spectra, while the data of the $NiSi_2$ Ni L_3 transition display a definite disagreement between theory and experiment, both in the energy location of the main structures and in the shape of the spectrum. The presence of the hole strongly modifies the intensity of the spectra with respect to the ground-state calculation, but neither the curve computed from the FS rule[2] (full line) nor the initial-state calculation (dashed line), suggested by the HF approach,[3] agrees with the experimental spectrum when the process occurs on the metal atom. Similar disagreement has been previously found by Zeller in bcc transition metals.[20] The data of Fig. 2 show unambiguously that the FS rule, corresponding to the core-hole excited-atom calculations, describes the measured data for Si rather well, but not the absorption from the metal atom.

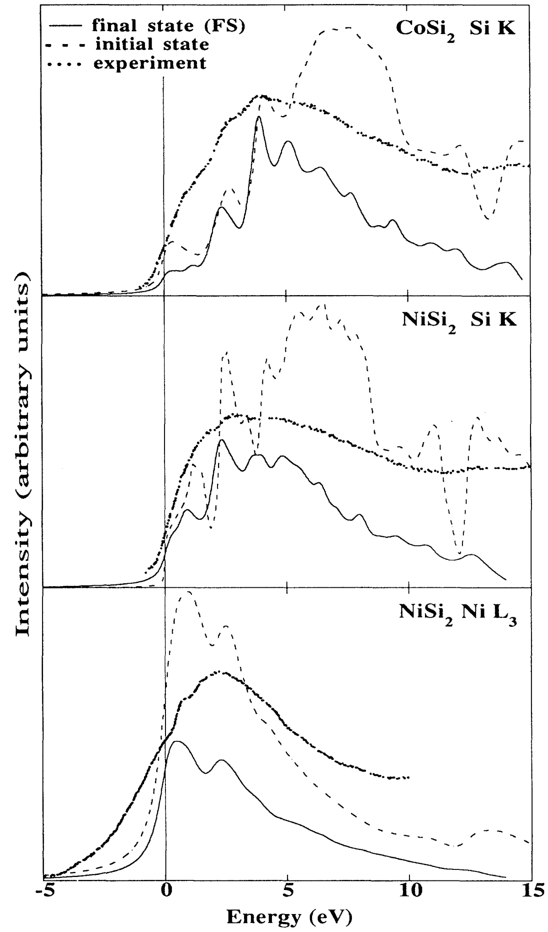

FIG. 2. Comparison between the experimental (dotted curve) and theoretical x-ray absorption spectra. Full lines show the results according to the final-state rule (core-hole excited-atom calculation), while dashed lines refer to the ground-state case. Upper panel: $CoSi_2$ Si K absorption (experimental data from Ref. 10); central panel: $NiSi_2$ Si K absorption (experimental data from Ref. 10); lower panel: $NiSi_2$ Ni L_3 absorption (experimental data from Ref. 11). Energies (in eV) are referred to the threshold E_F (vertical line).

In conclusion we have shown that (i) a single-particle picture can be partially applied to complex materials like crystalline $CoSi_2$ and $NiSi_2$, where free and localized electrons are both present; (ii) the best prescription is provided by the final-state rule;[2] (iii) the FS rule works only for processes concerning *s-p* bonded atoms, since the presence of localized *d* states has a dramatic effect and the dynamical distortion of the spectrum invalidates the single-particle scheme.

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