RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 28, NUMBER 6 15 SEPTEMBER 1983

Atomic nature of the $L_{\mathrm{II,III}}$ white lines in Ca, Sc, and Ti metals as revealed by resonant photoemission

J. Barth,* F. Gerken, and C. Kunz
II. Institut für Experimentalphysik, Universität Hamburg, D-2000 Hamburg 50, West Germany

(Received 23 March 1983; revised manuscript received 11 July 1983)

The valence-band photoemission of Ca, Sc, and Ti is shown to be resonantly enhanced for excitation energies in the $L_{\mathrm{II,III}}$ white lines. This favors an atomic approach to the line shape and intensity ratio of the white lines over the band-structure approach, which was recently found to be at variance with experiments.

The structure observed above x-ray absorption edges is attributed to two different origins. The near-edge structure within the immediate vicinity of the edge is interpreted in terms of the density of empty valence states available for the excited electron, while the extended absorption fine structure arises from the interference of the photoelectron's wave function with its part backscattered at the neighboring atoms, which modulates the matrix element for the electronic transition. The near-edge structure becomes particularly interesting for $L_{\mathrm{II,III}}$ edges in transition metals, where optical absorption probes the empty d-valence states. In these cases prominent resonances, referred to as "white lines," are observed. Recently it has become feasible to calculate absorption spectra from the threshold up to ~150 eV above the edge using a band-structure-based single-particle calculation.[1] For a large variety of systems, these calculations match experimental results strikingly well; small though persistent discrepancies between the placement of structures are attributed to the presence of the core hole.[2,3] Yet, there are also outstanding examples for complete failure of a band-structure-based explanation, namely, the $L_{\mathrm{II,III}}$ edges of $3d$ transition metals.[3] In these cases, the line shapes and intensity ratios of the white lines bear no obvious relation to calculated densities of d-band states.[3,4] On the other hand, resonances in the vicinity of $3p$ absorption edges of the $3d$ metals which occur in the soft-x-ray region have been explained on the basis of quasiatomic discrete transitions into $3p^5 3d^{N+1}$ multiplet states.[5,6] The discrete nature of the excited state interfers with the $3d \rightarrow \epsilon l$ continuum via a Super-Conig-Kronig decay $3p^5 3d^{N+1} \rightarrow 3p^6 3d^{N-1} \epsilon l$ (direct recombination) leading to a Fano-type[7] line shape in the absorption curve[6] and to prominent resonances in the $3d$-photoemission cross section.[8]

In view of the two alternative interpretations of x-ray absorption resonances we have applied the technique of resonance photoemission measurements to the $L_{\mathrm{II,III}}$ white lines of calcium, scandium, and titanium. By this means we have been able to provide support for the atomic interpretation for the investigated cases. General implications will also be discussed.

Experiments were carried out at the Hamburger Synchrotronstrahlungslabor (HASYLAB) using the grazing incidence monochromator FLIPPER.[9] Samples were prepared by evaporation from tungsten baskets in the spectrometer chamber at a base pressure of 1×10^{-10} Torr. The quality of the samples was checked by Auger and photoemission spectroscopy at low photon energies. For Ca, we detected Na as impurity, Sc and Ti samples were slightly contaminated by Cl, and the coverage was estimated to a few percent of a monolayer. The photoelectric yield of the samples was measured in "constant final state (CFS)" spectroscopy,[10] the final state being ~5-eV photoelectron kinetic energy. Under these conditions CFS spectra reflect the absorption cross section.[10] The $3d$-photoemission intensity was obtained by "constant initial state (CIS)" spectroscopy,[10] the initial energy being set to the valence band. No corrections are applied to the measured spectra. The primary intensity of the monochromator cannot be determined accurately in this energy range. It is expected, however, to vary smoothly with photon energy.[9] Because the relative energy variation of our measurements covering the $L_{\mathrm{II,III}}$ white lines is very small, the raw data yield photoemission intensity variations reasonably well without corrections.[11]

The $L_{\mathrm{II,III}}$-absorption edges of the $3d$ metals have very rarely been studied and, because of severe experimental difficulties for both optical and electron-energy-loss measurements, the detailed line shapes could not be resolved until recently (see Refs. 4 and 12 and references therein). The improved FLIPPER monochromator at HASYLAB provides reasonably high photon flux at sufficient resolution to allow optical studies of the white lines up to Ti including even the investigation of energy-resolved photoemission. Yield spectra of the white lines of Ca, Sc, and Ti are displayed in Fig. 1; the energy positions of the maxima are given in Table I. The result for Ti is directly comparable with the energy-loss measurement of Leapman and Grunes[4] and the quantum-yield measurement of Sivkov and Vinogradov.[12] The energy scale of the present experiment exhibits a displacement of ~1 eV. This is in the order of uncertainty for the energy calibration of our monochromator at high photon energies. For Ca and Sc the white lines fall within a region of higher accuracy of energy calibration. Here, the onsets of $2p$ ab-

TABLE I. Energy positions of the $L_{\mathrm{II,III}}$ white lines in eV.

	This work		Reference data	
Ca	348.2	351.6	349.27	352.54[a]
Sc	401.7	405.9		
Ti	456.8	462.0	458	464[b]
			457.7	463.0[c]

[a] Optical absorption of Ca vapor, Ref. 13.
[b] Energy loss of Ti metal, Ref. 4.
[c] Optical absorption of Ti metal, Ref. 12.

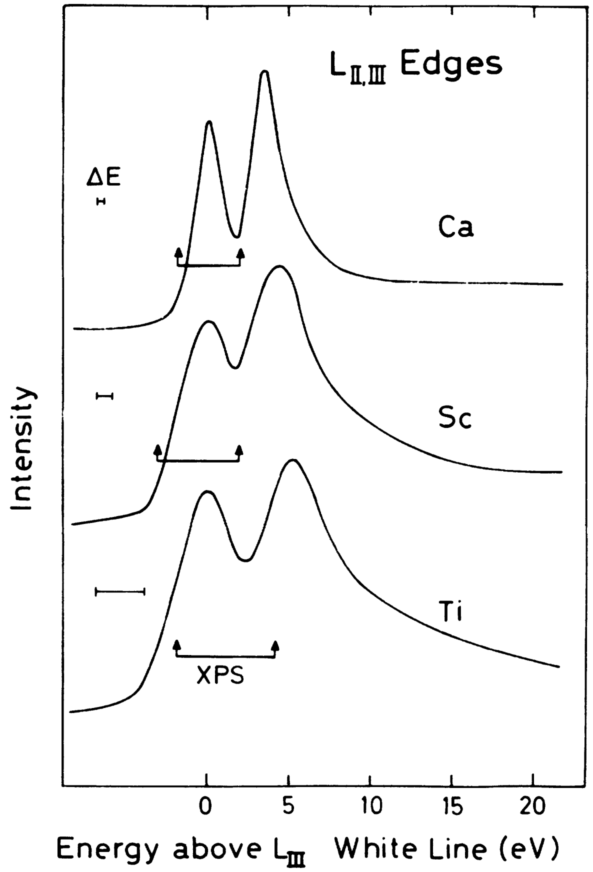

FIG. 1. Photoelectric yield of Ca, Sc, and Ti at the $L_{\mathrm{II,III}}$ absorption edges. ΔE denotes the energy resolution of the monochromator; the arrows mark the $2p$ binding energies from x-ray photoemission spectra (Ref. 14).

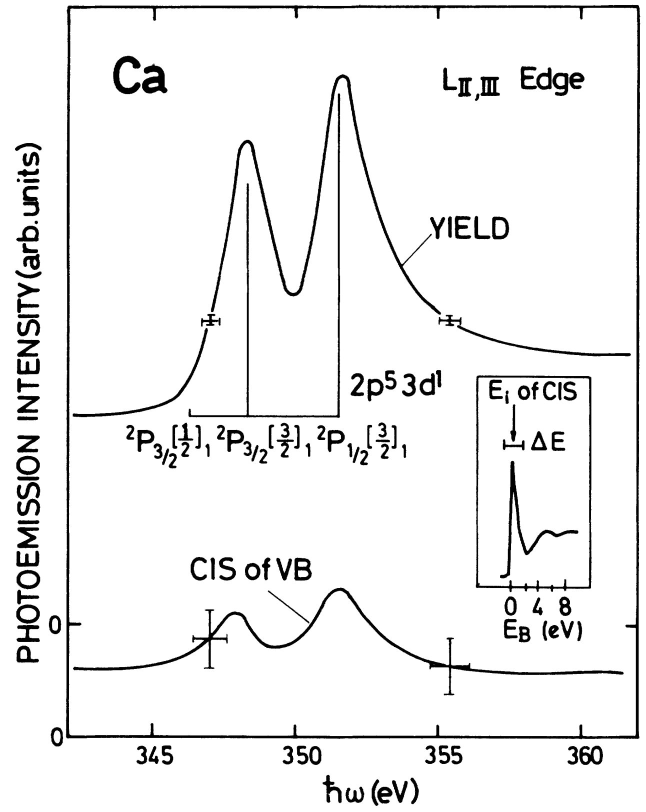

FIG. 2. Upper part: Yield spectrum of the $L_{\mathrm{II,III}}$ edge of Ca metal compared to calculated intensities of the optical transition $2p^6 3d^0\,{}^1S_0 \rightarrow 2p^5 3d^1$ (Ref. 13). The energy of the calculated transitions is shifted according to the yield spectrum; the energy splitting is retained. Lower part: CIS spectrum of the valence band with initial energy setting and total energy resolution as shown in the insert relative to an energy distribution curve at $\hbar\omega = 50$ eV. Vertical bars of yield and CIS spectrum give the noise of the curves obtained with a recorder, horizontal bars give the monochromator's energy resolution.

sorption coincide with the $2p$ binding energies in x-ray photoemission[14] (see Fig. 1). Shifting the Ti yield spectra corresponding to the energy reported in the literature[4,12] leads to the same result.

We make no attempt to deconvolute the L_{III} and L_{II} white line because this requires ambiguous assumptions concerning the shape of the $2p$ continuum excitation. It is, however, obvious already from the yield spectra of Fig. 1 that, equivalent to the finding of Leapman and Grunes,[4] the intensity ratio between the L_{III} and L_{II} line is far from the 2:1 statistical ratio of the two spin-orbit split $2p$ core-hole states. According to a band-structure calculation, deviations of the white-line intensity ratio from the 2:1 statistical ratio are basically negligible.[1] On the other hand, in an atomic interpretation of the white lines at $2p^5 3d^{N+1}$ multiplet states, the 2:1 statistical ratio is only expected in the limit in which the core-hole spin-orbit interaction is much larger than the electrostatic direct and exchange interactions between the hole and the $3d$ electrons.[15] In the case of calcium, the calculation of absorption intensities is easy because the optical selection rules allow transitions only into ^1P final states out of the ^1S ground state (LS coupling adopted). Mansfield fitted a term-dependent Hartree-Fock calculation in the intermediate coupling scheme to his $2p$ absorption measurement of Ca vapor.[13] The result is in excellent agreement also with the present $2p$ yield of metallic Ca (Fig. 2, upper part).

Coupling between the core hole and the excited electron can finally be proven by the detection of a direct recombination between them resulting in a resonance of outer-shell photoemission. In fact, we observe such a resonance for the valence-band emission separated from an LVV Auger transition (V for valence band) which bears no evidence for an electron-hole coupling (Fig. 2, lower part). To obtain a sufficient intensity for a CIS spectrum of the valence band, only a moderate resolution could be reached. In the insert of Fig. 2 the combined energy resolution ΔE of monochromator and electron analyzer is indicated relative to an energy distribution measurement of the valence-band photoemission at 50-eV photon energy. For measurements within the white-lines region we sample the photoemission up to 2 eV below the Fermi level. Since the measured widths of the resonances are more than twice as large, they cannot exclusively be explained by an LVV Auger transition which may only influence the low-energy part of the measured resonance profile. This result is corroborated by energy distribution curves obtained at excitation energies within the region of the white lines.

Equivalent results are found for Sc and Ti. The intensity ratio between the maxima of the valence-band resonances shows increasing deviations from the white-lines intensity ratio, which we explain by the $L_{\text{II}}L_{\text{III}}V$ Auger transition concurring with the direct recombination decay of a L_{II} hole. This Auger process becomes increasingly important with increasing d-band filling as is showcased by the larger width of the L_{II} white lines. Our result for Ti is shown in Fig. 3.

Our results demonstrate that atomiclike resonances due to intershell interactions are not confined to the thresholds of the outermost p-symmetric core levels. This raises the question of how a prediction can be achieved whether an atomic approach is in favor of a band-structure approach to interpret x-ray absorption edges. The answer is usually given in terms of the spatial overlap between core- and valence-electron wave functions.[16] Here let us translate this into a discussion of Auger processes determining the lifetime of the excited state. Consider an excitation of a core $2p$ electron (A) into empty valence d states (V). For these excitations, a band-structure approach should be considered only if the lifetime of the excited electron is sufficiently large to probe the environment of the excited site in the solid. However, if the excited state decays by a fast Auger decay involving the valence d states (ABV decay) the final state will be indistinguishable from that of a direct photoemission of a B electron. In fact, this Auger process may be called direct recombination of an $A \rightarrow V$ resonance excitation, and its matrix element governs the strength of the intershell interaction between the shells A and B.[17]

For the cases of interest, calculations of Auger lifetimes of resonantly excited configurations are not available in general.[18] Auger transition rates of core holes may only serve as a rough estimate. For Ti it has been calculated that valence d electrons participate with 20% in Auger decays of an L_{III} hole.[19] But the participation of valence d electrons increases strongly with increasing d band filling[19] so that the result for a $2p \rightarrow 3d$ resonance excitation may be significantly different. Yet, we readily recognize a trend in the strength of intershell interactions for deeper-and-deeper–lying core thresholds. An Auger decay involving the valence d states has to compete with more and more other Auger channels which makes intershell interactions less likely. Accordingly, Materlik, Müller, and Wilkins have recently been able to explain the $L_{\text{II,III}}$ white lines of rare-earth metals within a band-structure approach.[2] In this context, the earlier observation of Wei and Lytle of a Fano-type asymmetry present in the $L_{\text{II,III}}$ white lines of Ta (Ref. 20) remains an unresolved problem. Note, however, that interference effects may also arise for two-hole final states as showcased by the satellite resonances at the $3p$ edges of Ni, Cu, and Zn. It may thus be speculated that the Auger decay of the Ta $L_{\text{II,III}}$ white lines could interfere with double vacancy productions of the outer-shell absorption. This problem clearly deserves further investigation.

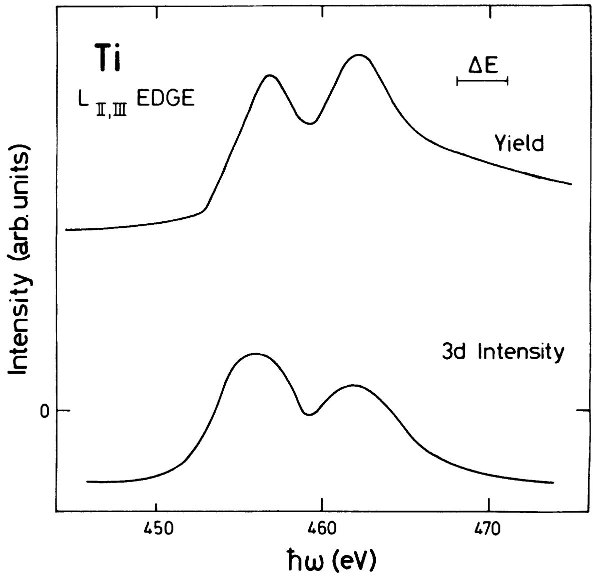

FIG. 3. Yield spectrum and CIS spectrum of the valence band of Ti in the region of the $L_{\text{II,III}}$ edges. ΔE denotes the energy resolution of the monochromator.

In conclusion, we have demonstrated that the $L_{\text{II,III}}$ white lines of Ca, Sc, and Ti must be interpreted as quasiatomic excitations of $2p^5 3d^{N+1}$ multiplet states. For Ca, the absorption agrees well with a term-dependent Hartree-Fock calculation in intermediate coupling by Mansfield,[13] and further detailed theoretical investigation is under progress.[21] The presence of intershell interactions is observed in all investigated cases. The general need for calculated Auger lifetimes of excited configurations in transition metals has been pointed out in order to achieve a prediction of whether x-ray absorption edges of p-symmetric core levels should be interpreted in an atomic or band-structure approach.

ACKNOWLEDGMENTS

This work is supported by the Bundesministerium für Forschung und Technologie from Funds for Research with Synchrotron Radiation.

---

*Present address: Quantum Metrology Group, National Bureau of Standards, Washington, D.C. 20234

[1] J. E. Müller, O. Jepsen, and J. W. Wilkins, Solid State Commun. 42, 365 (1982).

[2] G. Materlik, J. E. Müller, and J. W. Wilkins, Phys. Rev. Lett. 50, 267 (1983).

[3] L. A. Grunes, Phys. Rev. B 27, 2111 (1983).

[4] R. D. Leapman and L. A. Grunes, Phys. Rev. Lett. 45, 397 (1980).

[5] J. L. Dehmer, A. F. Starace, U. Fano, J. Sugar, and J. W. Cooper, Phys. Rev. Lett. 26, 1521 (1971).

[6] R. E. Dietz, E. G. McRae, Y. Yafet, and C. W. Caldwell, Phys. Rev. Lett. 33, 1372 (1974); L. C. Davis and L. A. Feldkamp, Solid State Commun. 19, 413 (1976).

[7] U. Fano, Phys. Rev. 124, 1866 (1961).

[8] J. Barth, F. Gerken, K. L. I. Kobayashi, J. H. Weaver, and B. Sonntag, J. Phys. C 13, 1369 (1980).

[9] J. Barth, F. Gerken, C. Kunz, and J. Schmidt-May, Nucl. Instrum. Methods 208, 307 (1983).

[10] C. Kunz, in *Photoemission in Solids II*, edited by L. Ley and M. Cardona (Springer, Berlin, 1979).

[11] J. Barth, F. Gerken, and C. Kunz, Nucl. Instrum. Methods 208, 797 (1983).

[12] V. N. Sivkov and A. S. Vinogradov, Fiz. Tverd. Tela (in press) [Sov. Phys. Solid State (in press)].

[13] M. W. D. Mansfield, Proc. R. Soc. London, Ser. A 348, 143

(1976).

[14] See data compilation of L. Ley and M. Cardona, Ref. 10.

[15] I. I. Sobel'man, *Atomic Spectra and Radiative Transitions* (Springer, Berlin, 1979).

[16] G. Wendin, in *X-ray and Atomic Inner-Shell Physics—1982,* AIP Conf. Proc. No. 94, edited by B. Crasemann (American Institute of Physics, New York, 1982), p. 495.

[17] Y. Yafet, Phys. Rev. B 21, 5023 (1980); 23, 3558 (1981).

[18] For the Mn $3p$ resonance, such a calculation has been carried out; see L. C. Davis and L. A. Feldkamp, Phys. Rev. A 17, 2012 (1978).

[19] E. J. McGuire, Phys. Rev. A 3, 1801 (1971).

[20] P. S. P. Wei and F. W. Lytle, Phys. Rev. B 19, 679 (1979).

[21] J. Barth, F. Gerken, C. Kunz, and G. Wendin (unpublished); G. Wendin (unpublished).