Multielectron transition effects on x-ray-fluorescence spectra

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In this work, measurements of the $K\alpha$ line from pure samples (Z = 20, 22, and 23), using synchrotron radiation of different energies, were carried out. Experimental evidence of the presence of double K holes and their effects on x-ray-fluorescence spectra is reported. The influence of multielectron transitions in calculations related to spectrochemical analyses is discussed.

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I. INTRODUCTION

The multielectron transition (MET) is an atomic process where more than one electron changes state, involving the absorption or emission of one photon. This effect was predicted as early as 1925 by Heisenberg [1]. It was later formulated by Ritchmeyer [2] and Condon [3], and the selection rules were presented by Goudsmit and Gropper [4].

The various types of MET's include the one-photon–two-electron (OPTE) excitations, two-electron–one-photon (TEOP) decay, and other transitions. A review of the types of MET's has been presented by Åberg [5].

One-photon–multielectron evidence was not found until the mid-1960s. These works reported double photoionizations in the x-ray absorption spectra of inert gases [6, 7]. Only during the past decade was it possible to detect multiple ionizations in solids [8–10].

Two-electron–one-photon evidence was first found in 1975, to our knowledge, by Wölfli *et al.* [11] during studies on heavy-ion–atom collisions. Since then, several particle-based collision experiments (heavy-ion–atom, proton-atom, and also electron-atom) have reported similar results [12–14].

During the 1980s, several papers reporting multiple photoionizations at core levels of solids were published [8–10]. Most of these works dealt with double or triple vacancies $1s^{-}+2s^{-}$, $1s^{-}+2p^{-}$, $1s^{-}+2s^{-}2p^{-}$, $1s^{-}+3p^{-}$, but only a few faced the double transition at the $1s$ level (two vacancies in the K shell).

In regard to this particular transition, Salem and Kumar [15] performed absorption experiments to determine the ratio

$$R_{K--}=\frac{\sigma_K^{--}}{\sigma_K^{-}}, \tag{1}$$

where σ_K^{--} represents the double K-photoionization cross section and σ_K^{-} denotes the single K-photoionization cross sections. They found it to be 3.2×10^{-3} for Cu. Ahopelto, Rantavuori, and Keski-Rahkonen [16], during studies on hypersatellite line intensities, reported 6.9×10^{-4} for Ti and 5.5×10^{-4} for Fe.

When multiple vacancies are created, the process by which these vacancies are filled is slightly different from the single-decay transition. Spectator vacancies in levels higher than that of the deepest hole produce the so-called *satellite* lines. In the case of double vacancies at the $1s$ level (two holes in the K shell), sequential transitions give place to characteristic emissions known as *hypersatellite* lines, denoting $K\alpha^h$ the $2p\rightarrow1s^{--}$ transitions.

Regarding the determination of radiative decay probabilities (fluorescence yields) of satellite and hypersatellite lines, several papers have been published [17,18]. In addition, the influence of the atomic configuration on the fluorescence yield coefficient has been dealt with by Larkins [19] and Hartmann [20], among others.

In a recent paper, Chen [21] has calculated the fluorescent yield coefficient for double K-hole states of elements with $10<Z<36$, using the multiconfiguration Dirac-Fock method. He found that the ratio of the K-shell fluorescence yields for double-vacancy states to the single K-hole state increases by 33% for Z = 10, and by about 3% for Z = 36. Tunnell and Bhalla [17] calculated this ratio to be 0.888 for Ne and 0.931 for Si. Figure 1 shows an interpolation of the double K-hole data reported by Chen, compared with the single K-hole fluorescence yield compiled by Scofield [22].

Double K vacancies also affect the emission probabilities Γ_K, the ratio of $K\alpha$ to $K\beta$, as pointed out by Benka [23] in 1980. Recently, Lorenz and Hartmann [24] found that the $K\alpha$-to-$K\beta$ ratio of Ag for the double K-hole states increases by 5% with respect to the single K-hole state.

It should be pointed out that all the mentioned effects increase as the atomic number decreases.

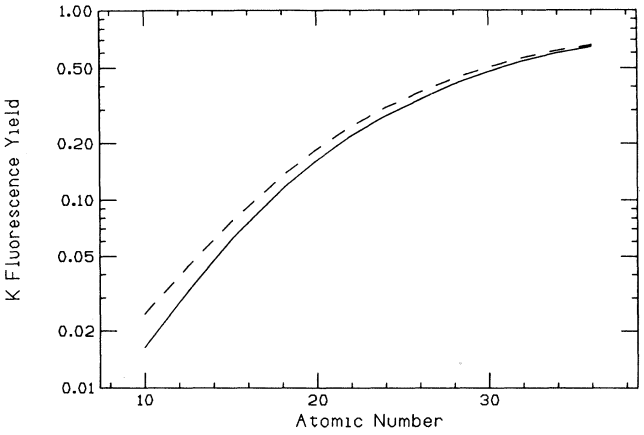

FIG. 1. Interpolation of the double K-hole data reported by Chen [21], compared with the single K-hole fluorescence yield compiled by Scofield [22].

The aim of this work is to analyze the influence of multiple transitions, in particular double K-photoionizations, on x-ray-fluorescent spectra.

II. DOUBLE K-PHOTOIONIZATION MEASUREMENTS

First, it should be mentioned that until 1991 all the experiments related to producing and detecting multiple vacancies had been performed on wavelength-dispersive systems [15, 16]. Although a few works used coincidence techniques in internal conversion experiments [25], no energy-dispersive setups have been used, to the authors' knowledge.

The production of fluorescent photons from an excited (pure) sample is determined by the probability of emission of a p-line fluorescent photon, $Q_p(\lambda)$, defined as follows [26]:

$$Q_p(\lambda) = \tau(\lambda)\omega_p\Gamma_p\kappa_p, \tag{2}$$

where $\tau(\lambda)$ is the mass photoabsorption coefficient of the sample to the wavelength λ, ω_p is the p-fluorescence yield, Γ_p is the p-line emission probability, and κ_p is the absorption p-edge jump. Some coefficients appearing in this factor are affected when double vacancies at the K level are present in the atom.

Double vacancies may occur if the exciting photons overcome the double-ionization K-edge energy given by [15]

$$E(1s^{--}) \simeq 2E(1s^{-}) + E(K\alpha_1^h) - E(K\alpha_1), \tag{3}$$

where $E(1s^{--})$ denotes the double-ionization K-edge energy, $E(1s^{-})$ is the single-ionization K-edge energy, $E(K\alpha_1^h)$ represents the $K\alpha_1$ hypersatellite line energy, and $E(K\alpha_1)$ is the $K\alpha_1$-line energy. According to the above, if the energy of excitation is higher than the double-ionization K-edge energy, then the $\tau(\lambda)$ will slightly increase its value. In presence of the double hole, the ω_K and Γ_K parameters will also increase. Since the product of these coefficients appears in the emission factor $Q_p(\lambda)$, the effects on the x-ray fluorescent line may be enhanced.

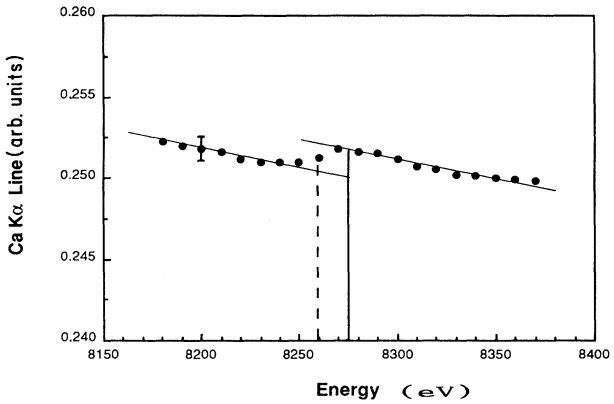

FIG. 2. Measured XRF $K\alpha$ intensities as a function of the incident energy (in eV) for Ca ($Z = 20$). Vertical lines show the measured (dotted line) and theoretical (solid line) double-ionization K-edge energies [15]. Solid lines among experimental points are only for reference and do not indicate data fitting.

Measurements of the $K\alpha$ line from pure samples were carried out in the Microanalysis Station of the PWA Group at the synchrotron facility of the Frascati National Laboratories [27] (INFN, Italy).

Radiation is emitted by the six-pole wiggler installed in the "ADONE" storage ring (1.5 GeV, 60 mA). The wiggler can reach a critical energy of 2.5 keV, producing 10^{14} (photons 1% bandwidth mm^2/sec). The incident beam is monochromated by means of a double Si(111) "channel-cut" crystal with about 3-eV resolution. The detecting system is a typical energy-dispersive setup in a reflecting geometry (45° + 45°). It consists of a Si(Li) solid-state

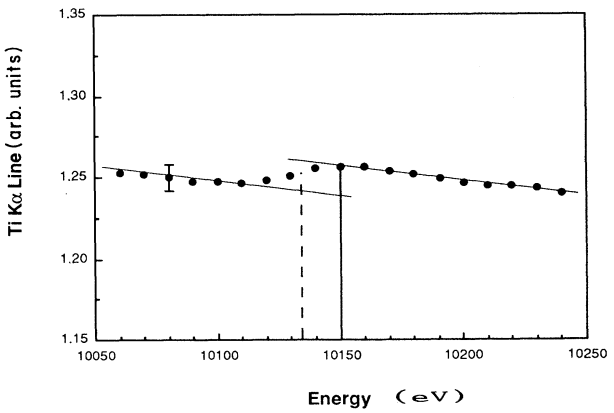

FIG. 3. Measured XRF $K\alpha$ intensities as a function of the incident energy (in eV) for Ti ($Z = 22$). Vertical lines show the measured (dotted line) and theoretical (solid line) double-ionization K-edge energies [15]. Solid lines among experimental points are only for reference and do not indicate data fitting.

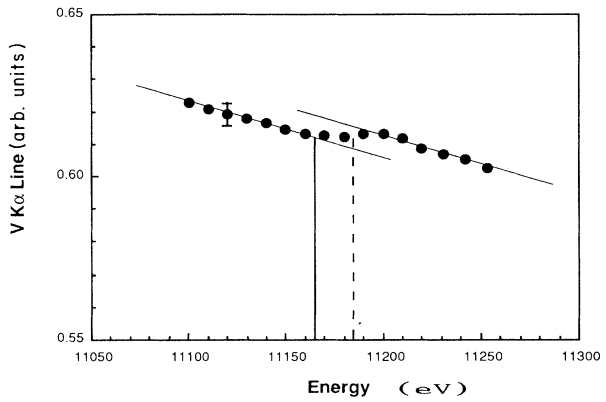

FIG. 4. Measured XRF $K\alpha$ intensities as a function of the incident energy (in eV) for V ($Z = 23$). Vertical lines show the measured (dotted line) and theoretical (solid line) double-ionization K-edge energies [15]. Solid lines among experimental points are only for reference and do not indicate data fitting.

detector of 180-eV resolution to the Mn $K\alpha$ line (^{55}Fe radioactive source), a fast amplifier, a 25-μsec analog-to-digital converter, and a $4K$-multichannel buffer.

Characteristic fluorescence photons from pure samples of Ca ($Z = 20$), Ti ($Z = 22$), and V ($Z = 23$) were measured. In order to investigate multielectron effects, an interval of incident energy centered at the double K-edge energy of each element was scanned. Peak intensities were calculated taking into account overlapped peaks, escape peak determinations, and peak-shape corrections. Figures 2–4 show the measured x-ray-fluorescence (XRF) $K\alpha$ intensities as a function of the incident energy for Ca, Ti, and V.

The jump energies agree with the theoretical values obtained from Eq. (3) as can be seen in Table I. These jumps are far from the extended x-ray absorption fine structure (EXAFS) region and cannot be considered anyway as an EXAFS oscillation.

The discontinuities observed in the figures represent almost 1% of the peak intensity (0.8% for Ca, 0.9% for Ti, and 0.8% for V). It is difficult to establish a comparison between the magnitude of the jumps measured in this work and the double K-photoionization cross sections reported by other authors [15, 16, 25, 28] since the measurements of this work take into account the contributions of emission probabilities and fluorescence yields. As mentioned in Sec. I the influence of double vacancies on these fundamental parameters is not well known.

TABLE I. Comparison between the measured double-ionization K-edge energies (in eV) and theoretical values.

Element	This work	Theory
Ca (20)	8260 ± 15	8275
Ti (22)	10135 ± 15	10150
V (23)	11185 ± 15	11165

III. DISCUSSION

It is clear that the jumps of the line intensities can affect later calculations if multielectron transitions are not taken into account. This would be particularly so, in the case of spectrochemical analysis, where concentrations are related to intensities. A small change in the measured line intensity may result in large changes in the concentrations, depending on the matrix elements of the sample.

As the theoretical support for spectrochemical analysis was developed many years ago, neither the fundamental parameter method [29] nor semiempirical methods to calculate concentrations take into account multiple vacancy effects.

Some remarks should be made on two-electron–one-photon decay. These transitions have always been observed in particle-atom collisions, since the probability of double photoionization (OPTE) followed by a TEOP decay is very small.

The probability, R_B, of the double decay relative to the probability of a sequential (single) decay has been calculated by Gavrila and Hansen [30], and Kelly [31]. They found $R_B = 5 \times 10^{-4}$ and $R_B \simeq 1.7 \times 10^{-4}$ for Fe. However, measurements carried out by Salem *et al.* [32] showed larger values than those, i.e., $R_B = 0.65$, for Fe and Co. Auerhammer *et al.* [33] found $R_B = 2.2 \times 10^{-3}$ for Al bombarded with 20-keV electrons. This value is about 100% larger than the one reported by Stoller *et al.* [34], in accordance with theoretical calculations.

Two-electron–one-photon transitions could result in the observation of ghost peaks (see figures in Refs. [14] and [33]) at the energy [14]

$$E(K\alpha\alpha^h) \simeq E(K\alpha^h) + E(1s^-) - E(2s^-). \quad (4)$$

Due to the low probability of observing TEOP with photon excitation, the effects of multiple decay on x-ray spectra are more likely to appear in electron microprobe experiments or proton-induced x-ray emission experiments, in both wavelength-dispersive and energy-dispersive setups.

IV. CONCLUSIONS

Double K photoionizations were detected using an energy-dispersive setup. The effects of double K holes, for the considered elements, represent almost 1% of the total $K\alpha$ line intensity. The magnitude of the jumps is larger than that considering only double K-photoionization cross section which indicates double-vacancy effects on fluorescence yields and emission probabilities.

Up to now, multielectron transitions have been observed in both wavelength-dispersive and energy-dispersive setups. The effects of multiple-vacancy photoionizations or multielectron decay can be detected and should be taken into account for a complete and correct analysis of the measured data. It is particularly important in the case of spectrochemical analysis, since numerical methods for deriving concentrations have become very sensitive to line intensities, but do not take

into account multiple transitions.

Although some characteristic parameters, such as hypersatellite energies, double-hole cross sections and energies, transition rates, etc., are now available, multielectron transitions are an open field; discrepancies between experiments and theory exist, and good numerical results and more theoretical works are long overdue.

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