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Measurement of K-line transition rates for Ti, V, Cr, Mn, Fe and Co using synchrotron radiation

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Abstract

Transition rates were obtained from spectra for pure metallic samples of atomic number ranging from 22 to 27, measured with monochromatic incident X-ray beams from a synchrotron source. The experimental setup for this consisted of an energy dispersive spectrometer in a conventional 45–45° geometry, mounted in an evacuated chamber. Absorption, detector efficiency and multiple scattering were taken into account. The results obtained are compared with recent theoretical and experimental data as well as with the well-known theoretical predictions from Scofield.

Keywords: Transition rates; Inner-shell ionisation; Synchrotron radiation; X-ray fluorescence

1. Introduction

The use of analytical techniques based on X-ray spectroscopy has been wide spread, especially because of their non-destructive character, and for the high efficiency achieved in characterizing a complete range of compositions—from major to trace element analysis—in quite short measurement times. Increasing technological advances have resulted in fast and accurate detection chains as well as the development of different excitation systems, which in turn allow for the optimization of detection efficiency. In addition, the introduction of new electronic devices allows complete automatization of measurements, complementing and enhancing the capabilities of the acquisition systems with high precision quantification programs, based on fundamental parameter methods.

When dealing with standardless techniques (see e.g. Trincavelli and Van Grieken, 1994), a very important parameter needed for quantitation algorithms is the transition rate, which gives the relative radiative decay probability once a vacancy has been generated in some inner-shell of the atom. Since in absolute methods no ratio is performed to compare sample intensities with the intensities from some standard, atomic parameters are not cancelled out. The same situation occurs when accounting for fluorescence enhancement effects (e.g., nickel in a copper matrix, where only the Cu-Kβ line can excite Ni–K shell), which may be strongly influenced by uncertainties in these magnitudes. On the other hand, absolute methods for the determination of film thicknesses may require accurate knowledge of these transition rates (Vázquez et al., 1990).

Considerable importance in having adequate knowledge of these transition rates concerns the accuracy of the information which may be obtained about atomic structure. Further importance concerns an ability to test the validity of models for screening potentials, statistical models or results obtained from self consistent methods for individual orbitals (Latter, 1955; Salvat et al., 1987), with subsequent description based on Slater determinants (Slater, 1951). Many assessments have been performed in this area in regard to transition rates, the most popular being the predictions given by Scofield (1974). In a more recent work, Jankowski and Polasik (1989) consider Breit and QED (self-energy and vacuum polarisation) corrections, not taken into account by Scofield. Discrepancies still exist between the different theoretical models in addition to those between

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experimental and predicted $K\beta/K\alpha$ X-ray intensity ratios. Khan and Karimi (1980) carried out a compilation of the experimental data available at the time. Recent measurements have been performed by Bé et al. (1998) using a conventional X-ray tube, also dealing with the inconvenience of scattering of the incident bremsstrahlung spectrum in the sample. In the present study, with the aim of obtaining reliable values for K-line ratios, a set of measurements for metallic samples has been performed with monochromatic incident X-ray beams generated with a synchrotron source at the *Laboratório Nacional de Luz Síncrotron* (LNLS, Brazil), avoiding the problems introduced by background fitting.

2. Experimental

K-line transition rates for atomic numbers ranging from 22 to 27 were determined by irradiating pure metallic samples (always above 99.95%). The experimental setup consists of an energy-dispersive spectrometer in a conventional 45–45° geometry, mounted on the X-ray diffraction (XRD) beamline of the LNLS, a simplified diagram of which can be seen in Fig. 1. The incident and fluorescent beams were collimated in order to reduce spurious contributions from radiation scattered in the sample/detector chamber walls.

The white synchrotron radiation beam was monochromatized by using a Si(1 1 1) double-crystal monochromator. Incident beams of energies ranging from 6.5 to 12.5 keV were used, and the fluorescent spectra were recorded with an Amptek XR100 Si PIN-diode detector.

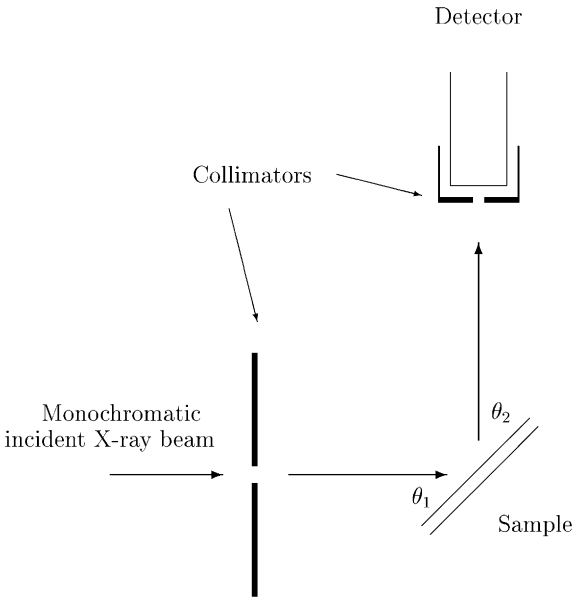

Fig. 1. Schematic diagram showing the experimental setup.

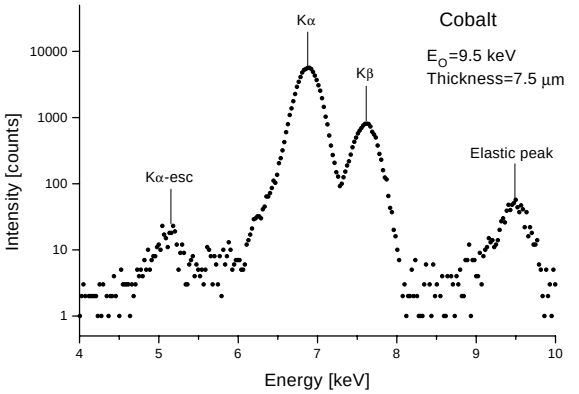

Fig. 2. Cobalt spectrum acquired for an incident beam energy of 9.5 keV. Notice the very low background only appreciable with logarithmic scale.

Table 1
Experimental conditions for the different samples measured

Element	Thickness (μm)	E_0 (keV)
Ti	7.5	7.0
V	7.5	8.0
Cr	10	6.5
Mn	10	10.5
Fe	10	10.2
Co	7.5	9.5

Samples and detector were mounted in a chamber evacuated to 0.1 mbar, in order to reduce absorption in the air. In addition, negligible background radiation was achieved, very low scattering occurring along the incident beam and fluorescence beam paths. As an example, Fig. 2 shows a typical spectrum for a pure cobalt sample, of thickness chosen to minimize the probability of multiple scattering. The list of elements, the corresponding film thicknesses and the incident beam energies used are displayed in Table 1.

3. Data processing and results

The recorded spectra were processed by means of the program AXIL (Van Espen et al., 1987). Measured and generated intensity ratios are related by means of the expression:

$$\left(\frac{I_\beta}{I_\alpha}\right)_{\text{meas}} = A\,\eta\left(\frac{I_\beta}{I_\alpha}\right), \tag{1}$$

where A takes into account the effect of absorption of the incident and Kα and Kβ fluorescent radiations, and η is the correction for detection efficiency. A dominant interest in techniques based on X-ray analysis is the ratio

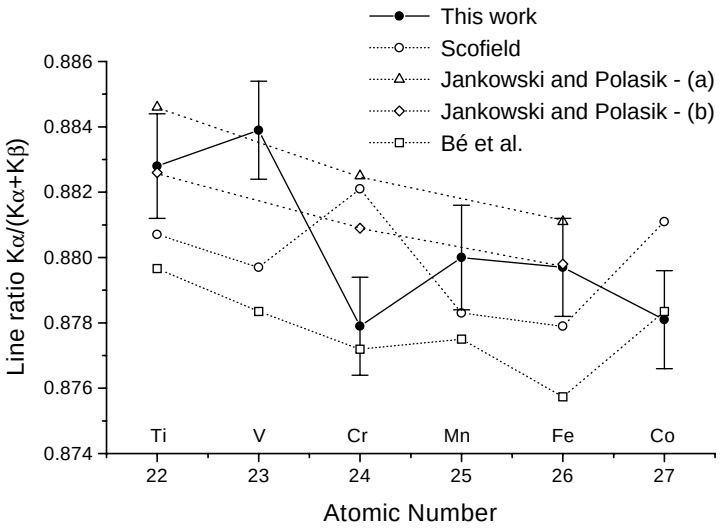

Fig. 3. Comparison of K transition rates obtained in this work with theoretical (Scofield, 1974; Jankowski and Polasik, 1989) and experimental data (Bé et al., 1998). The two results for Jankowski and Polasik correspond to: (a) Coulomb gauge and (b) Babushkin gauge.

between the Kα and total K characteristic intensities:

$$\zeta = \frac{1}{1 + I_\beta/I_\alpha} = \frac{1}{1 + (1/A\eta)\left(\frac{I_\beta}{I_\alpha}\right)_{\text{meas}}}. \quad (2)$$

Assessment of A is obtained through use of the well-known expressions for simple (single scattering) events:

$$A = \frac{1 - e^{-(g+b)t}}{g+b} \frac{g+a}{1 - e^{-(g+a)t}} \quad (3)$$

with $g = \mu(E_0)\sec\theta_1$, $a = \mu(E_\alpha)\sec\theta_2$, $b = \mu(E_\beta)\sec\theta_2$, t is the sample mass-thickness, $\mu(E)$ the mass-attenuation coefficient for the energy E, E_0 the incident energy, E_α and E_β are the characteristic energies of Kα and Kβ lines, respectively, and θ_1 and θ_2 the angles of incident and outgoing fluorescent radiation, respectively.

The contribution of multiple scattering events was evaluated by means of a method proposed by Tirao and Stutz (2003), revealing negligible effects for all of the cases analysed. The least favourable situation studied in this work was that for Cr, for which second order processes contributed 1.08% and 1.12% of the primary Kα and Kβ-line intensities, respectively. Thus, the correction associated with second order processes would amount to only 0.005%, being much smaller than the experimental errors.

The detection efficiency for fluorescence lines $j = \alpha, \beta$ took into account not only attenuation in the entrance window and layers of the detector, but also for losses due to the finite thickness t_{Si} of the active Si layer:

$$\varepsilon_j = \exp\{-[\mu_{\text{Be}}(E_j)t_{\text{Be}} + \mu_{\text{Au}}(E_j)t_{\text{Au}} + \mu_{\text{Si}}(E_j)t_{\text{DL}}]\} \times \{1 - \exp[-\mu_{\text{Si}}(E_j)t_{\text{Si}}]\} \quad (4)$$

where the first exponent accounts for losses in the beryllium window, gold contact and dead layer (DL), and the second exponent represents the probability of a photon being absorbed in the active volume. The corrections $\eta = \varepsilon_\beta/\varepsilon_\alpha$ on the line ratios in no case exceeded 1%.

Even though escape peaks were observed in some spectra, their influence on the characteristic intensities was negligible, as can be seen in the example given in Fig. 2.

The experimental error assigned to each line ratio was assessed by propagating the uncertainties of characteristic peak intensities in expression (2). The values obtained for the transition rates are shown in Fig. 3, as well as a comparison to theoretical data from Scofield (1974) and Jankowski and Polasik (1989) and recent experimental results obtained by Bé et al. (1998). The values of the last reference are based on their "special average level (SAL)" scheme for generating one-electron wave functions, using two gauge conventions: (a) Coulomb and (b) Babushkin (see, e.g., Grant, 1974). As can be seen, our results are spread around the theoretical predictions, whereas the data given by Bé et al. systematically lie below them. Although Jankowski and Polasik state that in this atomic number range the Coulomb gauge gives better predictions, it is worth noticing that our results appear to be closer to those corresponding to the Babushkin gauge. However, theoretical predictions should be gauge invariant if exact wave functions were used; but, since only numerical atomic wave functions are available, results may depend on the gauge chosen (Chen and Crasemann, 1983).

4. Conclusion

Transition rates for K lines were determined using synchrotron X-rays as excitation source, in an experimental setup specially designed for minimizing secondary effects: absorption, multiple scattering, elastic and inelastic scattering for the incident and fluorescent radiation, with consequent reduction of the intensity of spurious continuous radiation under the peaks. The values obtained lie between both of the theoretical predictions considered. Further measurements should be carried out in order to reduce the experimental error, and therefore to be able to judge the reliability of the different theoretical models.

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