

Chemical effect on the K shell fluorescence yield of Fe, Mn, Co, Cr and Cu compounds

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Abstract. Chemical effects on the K shell fluorescence yields of Fe, Mn, Co, Cr and Cu compounds were investigated. Samples were excited using 59.5 keV energy photons from a ^{241}Am radioisotope source. K X-rays emitted by samples were counted by a Si(Li) detector with a resolution 160 eV at 5.9 keV. Chemical effects on the K shell fluorescence yields (ω_K) for Fe, Mn, Co, Cr and Cu compounds were observed. The values are compared with theoretical, semiempirical fit and experimental ones for the pure elements.

Keywords. Fluorescence yield; 3d elements; chemical effect.

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1. Introduction

The fluorescence yield of an atomic shell or subshell is defined as a probability that a vacancy in that shell or subshell is filled through a radiative transition. The fluorescence yield of a shell is equal to the number of photons emitted when the vacancies in the shell are filled, divided by the number of primary vacancies in the shell. A vacancy in an atomic inner shell decays rapidly through a cascade process composed of radiative and non-radiative emissions. Among these emissions, one of the most relevant is the X-ray fluorescence owing to its high occurrence and its useful applications. Fluorescence yield values play an important role in a variety of fields such as atomic physics, X-ray fluorescence analysis, health physics and industry.

Some studies [1–4] on L shell fluorescence yield (ϖ_L) have already been made. In recent years, K shell fluorescence yields for several elements [5–10], chemical effects on the K shell [11] and average L shell fluorescence yields [12,13] have been investigated by many authors. In the present study, chemical effects on K shell X-ray fluorescence yields for Fe and its compounds, Mn and its compounds, Co and its compounds, Cr and its compounds, Cu and its compounds are investigated.

2. Experimental measurements

The experimental set-up is shown in figure 1. 59.5 keV γ -rays from an ^{241}Am source are collimated on targets, each of thickness $100\text{--}300\ \mu\text{g}/\text{cm}^2$ of elements Fe, Mn, Co, Cr, Cu and of compounds FePO_4 , FeF_3 , Fe_2O_3 , $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$, $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$, $\text{FeCl}_3\cdot 2\text{NH}_4\text{Cl}\cdot \text{H}_2\text{O}$, $\text{Fe}(\text{SO}_4)_2\cdot \text{NH}_4\cdot 12\text{H}_2\text{O}$, $\text{MnSO}_4\cdot \text{H}_2\text{O}$, $\text{MnCl}_2\cdot 2\text{H}_2\text{O}$, $\text{MnCl}_2\cdot 4\text{H}_2\text{O}$, MnCO_3 , MnCl_4 , KMnO_4 , CoF_2 , CoF_3 , CoO , CoSO_4 , CoCl_2 , $\text{Co}(\text{SCN})_2$, $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$, $\text{CoSO}_4\cdot 7\text{H}_2\text{O}$, Co_2O_3 , $\text{Co}(\text{CH}_3\text{COO})_2$, $\text{Co}(\text{ClO}_4)_2\cdot 6\text{H}_2\text{O}$, Cr_2O_3 , CrCl_2 , CrCl_3 , $\text{Cr}(\text{NO}_3)_3$, $\text{Cr}_2(\text{SO}_4)_3\cdot \text{H}_2\text{O}$, $\text{Cr}_2(\text{SO}_4)_3\cdot \text{K}_2\text{SO}_4\cdot 24\text{H}_2\text{O}$, $\text{Cr}_3(\text{CH}_3\text{CO}_7)(\text{OH})_2$, CuCl , CuCl_2 , $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$, CuO , Cu_2O , CuCO_3 , CuC_2O_4 , CuCN , $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2\cdot \text{H}_2\text{O}$. All the targets have K edge energies lower than 59.5 keV. The fluorescent X-rays produced due to the interactions of the incoming photons with K shell electrons of the target elements are measured with a Si(Li) detector (resolution: 160 eV at 5.9 keV) and recorded using an ND 66B multichannel analyser system. The K X-ray spectra of Cu are shown in figure 2.

For measuring the K shell fluorescence yield, the intensity ratio of K X-rays to incoherent scattered X-rays was used. For this reason, aluminum was used as a scattering target. The K X-ray counting rate from the target of each element under study and the scattered radiation counting rate from the aluminum target, as measured by the detector is given by equations [10]

$$N(\text{K}) = R \frac{\Omega_1}{4\pi} \frac{N_A}{M_{(\text{K})}} t_{(\text{K})} W_i \beta_{(\text{K})} \sigma_{(\text{K})} \frac{\Omega_2}{4\pi} \varepsilon_{(\text{K})} \omega_{\text{K}}, \quad (1)$$

and

$$N(\text{Al}) = R \frac{\Omega_1}{4\pi} \frac{N_A}{M_{(\text{Al})}} t_{(\text{Al})} \beta_{(\text{Al})} \frac{d\sigma_{\text{KN}}(90^\circ)}{d\Omega} S(x, Z) \Omega_2 \varepsilon_{(\text{Al})}, \quad (2)$$

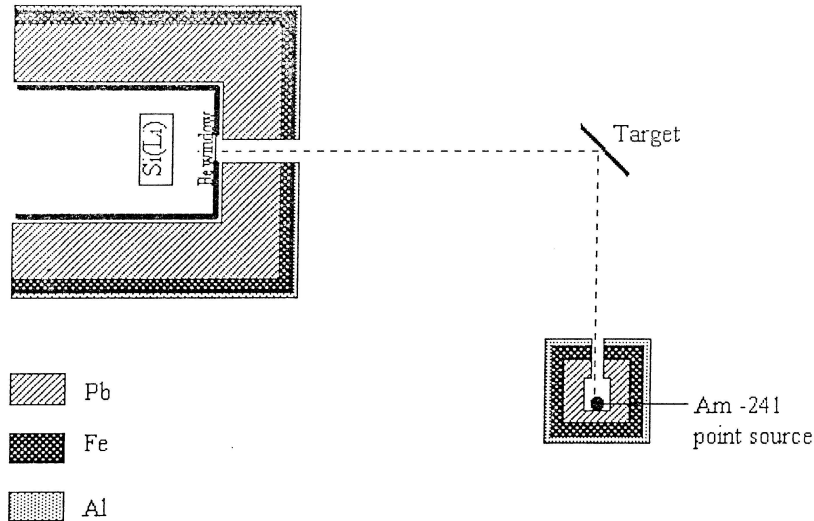


Figure 1. Experimental set-up.

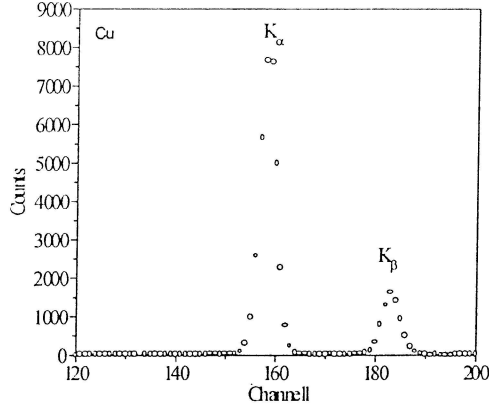


Figure 2. Spectra of Cu K X-rays.

where R is the source strength, Ω_1 is the source–target solid angle, W_i is the concentration in the target of the i th element, N_A is the Avogadro’s number, $M_{(K)}$ and $M_{(Al)}$ are the atomic weights of the target element and aluminum, $t_{(K)}$ and $t_{(Al)}$ are the thicknesses of the target and Al, σ_K is the K shell photoionization cross-section of the element at the excitation energy of 59.5 keV, ω_K is the K shell fluorescence yield, Ω_2 is the target–detector solid angle, $\varepsilon_{(K)}$ and $\varepsilon_{(Al)}$ are the detector efficiencies at the fluorescence and scattered X-ray energies, and $\beta_{(K)}$ and $\beta_{(Al)}$ are the absorption correction factors of fluorescent target and Al target. $(d\sigma_{KN}(90^\circ)/d\Omega)$ is the Klein–Nishina differential cross-section per electron and $S(x, Z)$ is the incoherent scattering factor of Al. From eqs (1) and (2), ω_K can be resolved:

$$\omega_K = \frac{M_K}{M_{Al}} \frac{t_{(Al)}}{t_{(K)}} \frac{\beta_{(Al)}}{\beta_{(K)}} \frac{\varepsilon_{(Al)}}{\varepsilon_{(K)}} \frac{N_{(K)}}{N_{(Al)}} \frac{4\pi}{W_i \sigma_K} \frac{d\sigma_{KN}(90^\circ)}{d\Omega} S(x, Z). \quad (3)$$

The $N_{(K)}$ and $N_{(Al)}$ values are determined from the photopeak and scattered peak areas at the same counting geometry, σ_K values were taken from the table of Scofield [14]. The differential Klein–Nishina cross-section per electron, $d\sigma_{KN}(90^\circ)/d\Omega$, is calculated using the well-known Klein–Nishina expression [15]. The function of $S(x, Z)$ vs. $x = \sin(\theta/2)/\lambda$ was determined for Al from the table of Hubbell *et al* [15]. The self-absorption correction factor for emitted K X-rays was determined by the following equation:

$$\beta_{(K)} = \frac{1 - \exp \left[- \left(\frac{\mu_\gamma}{\cos \theta} + \frac{\mu_K}{\cos \phi} \right) t_K \right]}{\left(\frac{\mu_\gamma}{\cos \theta} + \frac{\mu_K}{\cos \phi} \right) t_K}, \quad (4)$$

where μ_γ and μ_K are the total attenuation coefficients [16] at primary γ and emitted K X-ray energies, respectively, and θ ($=45^\circ$) and ϕ ($=45^\circ$) are the angles with the sample normal primary and emitted K X-rays. The $\beta_{(Al)}$ value is obtained similarly to eq. (4):

$$\beta_{(Al)} = \frac{1 - \exp \left[- \left(\frac{\mu_{\gamma(Al)}}{\cos \theta} + \frac{\mu_{s(Al)}}{\cos \phi} \right) t_{Al} \right]}{\left(\frac{\mu_{\gamma(Al)}}{\cos \theta} + \frac{\mu_{s(Al)}}{\cos \phi} \right) t_{Al}}, \quad (5)$$

where $\mu_{\gamma(Al)}$ is the absorption coefficient of aluminum at the energy of the incident γ -rays and $\mu_{s(Al)}$ is the absorption coefficient of aluminum at the scattered photons energy calculated using the Compton relation and a scattering angle of 90° .

The measured values of K shell fluorescence yield and the theoretical values [17,18] and semiempirical fits values [19,20] for pure elements are listed in tables 1 and 2. The relative difference (RD) between the experimental and Kostroun *et al* [17] values are presented in the last column in table 1. They were calculated using the equation,

$$RD = \frac{(\omega_K)_{\text{exp}} - (\omega_K)_{\text{theory}}}{(\omega_K)_{\text{theory}}} \times 100\%. \quad (6)$$

3. Results and discussion

In the method, the K X-ray counting rate from the target (eq. (1)) and the scattered radiation counting rate from the aluminum target (eq. (2)) are measured at the same geometry. From these equations, the K shell fluorescence yield, ω_K , is obtained (eq. (3)). The values of ω_K are independent of the primary photon flux and the source–target–detector geometry factor. The method also dispenses with the need for the determination of absolute values of source strength and solid angles. It can be seen from tables 1 and 2 that the present results are in good agreement for pure elements, within the experimental uncertainties. The estimated error in the experimentally measured ω_K value is $<6\%$ for this method. This error arises due to the uncertainties in various physical parameters, namely the errors in the evaluation of area under the K X-ray peaks, target thickness, detector efficiency and absorption correction factor.

Since the orbital energy of K, L, M, N shells and their subshells get closer to each other with increasing quantum number n , outer energy levels are sensitive to the chemical environment. Outer energy levels are strongly affected by ligands according to the crystal field theory. In addition to this, valence electrons participating in the formation of a chemical bond are removed from the atom and this effect causes a change in the electronic screening and a change in the outer shell binding energies. Thus, binding energies of K shell electrons are strongly affected by the chemical environment. Since K shell electrons have different binding energies in different compounds, Auger electron ejection probability and K shell fluorescence yield have different values for different compounds.

It has been shown that for the 3d transition metals the change in the number of 3d electrons is the only important contribution for the change in the K fluorescence yield values and the effect of changing 4s and 4p electrons can practically be neglected. The results of changes in the 3d electron population of all the transition metals in their compounds, one can either consider the rearrangement of electrons between 3d and 4s states of the transition metal or transfer of electrons from the 3d state to the ligand atom or vice versa. The chemical environment must be

Table 1. Experimental K shell fluorescence yield values.

Compounds	Exp.	RD	Compounds	Exp.	RD	Compounds	Exp.	RD
CuO	0.427 ± 0.028	-4.5	CrCl ₂	0.294 ± 0.009	+6.6	CoO	0.362 ± 0.008	+4.9
CuCl	0.423 ± 0.020	-5.4	CrCl ₃	0.295 ± 0.009	+6.9	CoF ₂	0.396 ± 0.010	+4.6
CuCl ₂	0.478 ± 0.033	+6.9	Cr ₂ O ₃	0.299 ± 0.010	+8.3	CoF ₃	0.397 ± 0.010	-4.3
CuCO ₃	0.481 ± 0.023	+7.5	Cr(NO ₃) ₃	0.298 ± 0.009	+8.0	Co ₂ O ₃	0.398 ± 0.009	+5.1
CuC ₂ O ₄	0.412 ± 0.020	-8.0	Cr ₂ (SO ₄) ₃ ·H ₂ O	0.301 ± 0.011	+9.1	Co(SCN) ₂	0.355 ± 0.007	-6.2
Cu ₂ O	0.470 ± 0.022	-5.0	Cr ₃ (CH ₃ CO ₇)(OH) ₂	0.315 ± 0.012	+14.3	Co(CH ₃ COO) ₂	0.352 ± 0.006	-7.0
CuCN	0.479 ± 0.022	+7.1	Cr ₂ (SO ₄) ₃ K ₂ SO ₄ ·24H ₂ O	0.321 ± 0.012	+16.4	CoCl ₂ ·6H ₂ O	0.416 ± 0.010	+9.8
Cu(C ₂ H ₃ O ₂) ₂ ·H ₂ O	0.514 ± 0.041	+14.8				CoCl ₂	0.399 ± 0.009	+5.4
CuCl ₂ ·2H ₂ O	0.496 ± 0.035	+10.9				CoSO ₄ ·7H ₂ O	0.412 ± 0.008	+8.8
						CoSO ₄	0.356 ± 0.007	-5.9
						Co(ClO ₄) ₂ ·6H ₂ O	0.422 ± 0.011	+11.6
MnCO ₃	0.285 ± 0.007	-7.8	FePO ₄	0.320 ± 0.010	-6.9			
MnCl ₄	0.326 ± 0.006	+5.2	FeF ₃	0.324 ± 0.012	-5.7			
MnSO ₄ ·H ₂ O	0.336 ± 0.009	+8.7	Fe ₂ O ₃	0.322 ± 0.010	-6.3			
KMnO ₄	0.289 ± 0.008	-6.5	FeCl ₃ ·6H ₂ O	0.371 ± 0.011	+8.1			
MnCl ₂ ·4H ₂ O	0.339 ± 0.013	+9.4	FeCl ₂ ·4H ₂ O	0.369 ± 0.012	+7.5			
MnCl ₂ ·2H ₂ O	0.335 ± 0.013	+8.1	FeCl ₃ 2NH ₄ Cl·H ₂ O	0.383 ± 0.013	+11.5			
			Fe(SO ₄) ₂ NH ₄ ·12H ₂ O	0.394 ± 0.013	+14.6			

Table 2. Theoretical and semiempirical fit values of K shell fluorescence yield.

Elements	Theoretical		Semiempirical fits		
	Kostroun [17]	Walters [18]	Hubbell [19]	Krause [20]	Bambynek [19]
Cu	0.448	0.467	0.441	0.440	0.454
Cr	0.276	0.293	0.286	0.275	0.289
Co	0.379	0.397	0.382	0.373	0.388
Mn	0.310	0.327	0.319	0.308	0.321
Fe	0.344	0.362	0.351	0.340	0.355

the real cause of the increase of the number of 3d electrons for Fe, Co, Cu, Cr and Mn in their compounds.

Our analysis shows that the changes of the K shell fluorescence yield values for Fe, Co, Cu, Cr and Mn in the compounds can be interpreted as due to changes in the electron population of the valence bands of Fe, Co, Cu, Cr and Mn in the compounds. We believe that the results of this study will be helpful to better understand the dependence of the K shell fluorescence yield values to changes in the valence electronic configurations of 3d transition metals and throw some light on the valence electronic structure of Fe, Co, Cu, Cr and Mn in compounds. Moreover, the results of this work can stimulate both the experimental and theoretical research with other 3d transition metal compounds.

It is observed that the experimental value deviates by as much as -6.3% for Fe_2O_3 , by $+14.6\%$ for $\text{Fe}(\text{SO}_4)_2\text{NH}_4 \cdot 12\text{H}_2\text{O}$, $+5.2\%$ for MnCl_4 , $+9.4\%$ for $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, -4.3% for CoO , 11.6% for $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, $+6.6\%$ for CrCl_2 , $+16.4\%$ for $\text{Cr}_2(\text{SO}_4)_3\text{K}_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$, -4.5% for CuO and $+14.8\%$ for $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$. This shows that when the number of atoms in a compound increases, significant differences between experimental and theoretical values are observed.

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