Measurements of K-shell fluorescence yields for Ti, V, Cr, Fe, Co, Ni and Cu elements and their halogen compounds

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Abstract

K-shell fluorescence yields ω_K were measured for the elements Ti, V, Cr, Fe, Co, Ni, Cu and F and Cl compounds of these elements. Measurements were carried out at 10 keV excitation energy using secondary excitation method. K x-rays emitted by samples were counted by a Si(Li) detector with 160 eV resolution at 5.9 keV. Measurement of K-shell fluorescence yields ω_K for these elements are compared with earlier experimental results obtained by other methods.

Key Words: X-ray, Fluorescence yield, Halogen compounds.

1. Introduction

The de-excitation of an atom with an inner-shell K vacancy can proceed either by the emission of an X-ray photon or by the ejection of Auger electrons. The de-excitation of an atomic shell is characterized by them fluorescence yields and is defined as the probability that a vacancy in the K-shell is filled through a radiative transition.

K-shell fluorescence yields ω_K are important for both basic and applied research. Measurements of fluorescence yields for different elements at various photoionization energies fulfil important tasks in atomic, molecular and radiation physics, elemental XRF analysis, medical research and irradiation processes. K shell fluorescence yields for different elements have been investigated for many years and have been compiled [1–3]. Theoretical values of ω_K were obtained in the region $4 \leq Z \leq 54$ by McGuire [4, 5] and Walters and Bhalla

[6] using the Hartree-Fock-Slater model. K-shell fluorescence yields of some elements were measured by using 59.54 keV γ-rays from a 100 mCi ^{241}Am radioactive source [7–9]. Although K-shell fluorescence yields ω_K have typically been studied for pure elements, a small number of studies have been concerned with chemical effects on K-shell fluorescence yield. X-ray emission spectra are influenced by the chemical combination of x-ray emitting atoms with different ligands. In the earlier studies by this group we investigated chemical effects on K-shell fluorescence yields [10, 11].

In the present investigation, the K-shell fluorescence yields for the elements Ti, V, Cr, Fe, Co, Ni, Cu, and F and Cl compounds of these elements have been measured at 10 keV x-ray excitation energy using a secondary excitation method.

2.   Experimental

We have measured the K-shell fluorescence yields ω_K for Ti, V, Cr, Fe, Co, Ni and Cu in TiF$_3$, TiF$_4$, VF$_3$, VCl$_3$, CrCl$_2$ CrF$_2$, CoF$_2$, CoF$_3$, CoF$_2$.4H$_2$O, CoCl$_2$, CoCl$_2$.6H$_2$O, NiF$_2$, NiF$_2 \cdots$ 4H$_2$O, NiCl$_2 \cdots$ 6H$_2$O, NiCl$_2 \cdots$ H$_2$O, NiCl$_2$, CuCl, CuCl$_2 \cdots$ 2H$_2$O, CuF$_2$, CuF$_2 \cdots$ 3H$_2$O. The samples were sufficiently thin such that no significant correction to the data was required for the difference of self-absorption between K$_\alpha$ and K$_\beta$ lines, but particle size corrections were nonetheless performed on the data. Powder samples were prepared by supporting on scotch tape. The secondary excitation method was used. The point source of ^{241}Am (100 mCi) excites the K x-rays from secondary exciter. The secondary excitation source was pure metal Ge (99.99%). The incident energies were calculated by taking the weighted average of K$_\alpha$ and K$_\beta$ x-ray energies according to their intensity ratios [12]. The Si(Li) detector, which has a resolution of 160 eV at 5.9 keV, and an ND66B pulse height analyzer were used to acquire K$_\alpha$ and K$_\beta$ photons emitted from samples. In order to determine how much Compton scattering photons contribute to the excitation of the sample, a reference secondary exciting sample having the same scattering properties with the sample was used in the same experimental conditions. Furthermore, the reference secondary exciting sample is so chosen only γ rays scattered from it can excite the main sample but not its secondary x-rays. To minimize the effect of the unwilling contribution of the Compton scattered photon, the peak area (originating from the scattered photons) obtained from this sample subtracted from the K$_\alpha$ and K$_\beta$ peak areas of the main sample.

The experimental set-up is shown in Figure 1. As shown, the lead shield avoided the direct exposure of the detector to radiation from the radioactive source. The angle of incident photons and emitted x-rays with respect to the normal to the surface of the sample was 45° in the present set-up. A typical K x-ray spectrum of NiCl$_2 \cdots$ 2H$_2$O is shown in Figure 2.
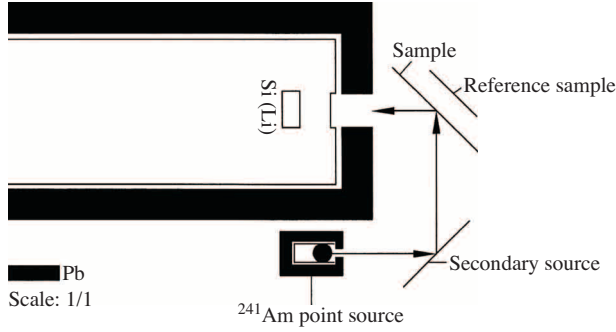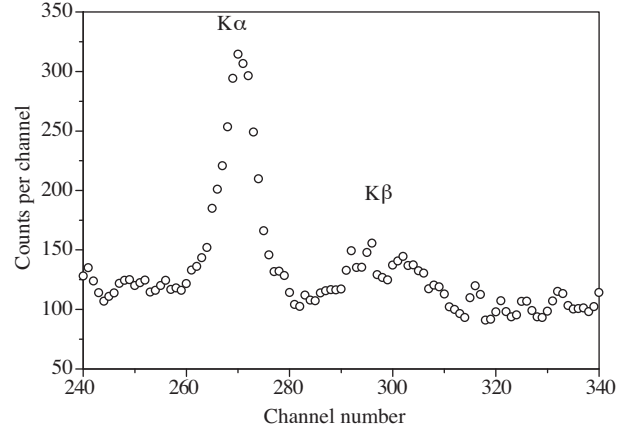
3.   Data analysis

3.1.   Theoretical method

Theoretical values of the K$_\alpha$ and K$_\beta$ x-ray fluorescence cross-sections (σ_{K_α}, σ_{K_β}) have been calculated using the relation,

$$\sigma_{K_\alpha} = \sigma_K^P(E)\omega_K f_{K_\alpha} \tag{1}$$

$$\sigma_{K_\beta} = \sigma_K^P(E)\omega_K f_{K_\beta}, \tag{2}$$

Figure 1. Experimental set-up.

Figure 2. K x-ray spectrum of $NiCl_2 \cdots 2H_2O$

where $\sigma_K^P(E)$ is the K shell photoionization cross-section for the given element at excitation energy E, ω_K is the K shell fluorescence yield and f_{K_α} and f_{K_β} are fractional x-ray emission rates for K_α and K_β x-rays, defined as

$$f_{K_\alpha} = (1 + I_{K_\beta}/I_{K_\alpha})^{-1} \tag{3}$$

$$f_{K_\beta} = (1 + I_{K_\alpha}/I_{K_\beta})^{-1}, \tag{4}$$

where I_{K_β}/I_{K_α} is the K_β to K_α x-ray intensity ratio. In the present calculations, the values of $\sigma_K^P(E)$ were taken from Scofield [13] based on Hartree-Slater potential theory, and the values of ω_K were taken from the tables of Krause [14]. I_{K_β}/I_{K_α} values based on relativistic Hartree-Slater theory were used for the evaluation of theoretical K XRF cross-sections [15].

3.2. Experimental

The K x-ray fluorescence cross-sections have been measured using the relation

$$\sigma_{Ki} = \frac{N_{Ki}}{I_0 G \varepsilon_i \beta_i t} \tag{5}$$

where N_{Ki} is the intensity observed for the K_i-th x-ray line of each given element, I_o is the intensity of exciting radiation, G is the geometry factor, t is the mass thickness of the element in the sample (in units of g•cm^{-2}), β_i is the target self absorption correction factor, correction factor (both for the incident and emitted radiation) and ε_i is the detection efficiency of the detector at the energy of Ki x-rays.

Values of $I_o G \varepsilon$ in the present experimental set-up were determined in a separate experiment. Targets of pure elements, having physical cross-section areas similar to those used in the main experiment, with atomic number $22 \leq Z \leq 29$, emitting fluorescent x-rays in the energy range 5.5–8.7 keV, were irradiated in the same geometry, and from which the emitted fluorescence x-rays were counted. $I_o G \varepsilon$ value for the present set up were determined by the following relationship [16–18],

$$I_0 G \varepsilon = \frac{N_{Ki}}{\sigma_{Ki} \beta_i m_i} \tag{6}$$

313

where N_{Ki} is the number of K_α and K_β x-rays recorded under the K_α or K_β peaks; σ_{Ki} is the σ_{K_α} or σ_{K_β} fluorescence cross-section.

The self-absorption correction factor β for both the incident and emitted radiation was calculated by using the expression

$$\beta = \frac{1 - \exp\left[-(\mu_{inc}/\cos\theta_1 + \mu_{emt}/\cos\theta_2)t\right]}{(\mu_{inc}/\cos\theta_1 + \mu_{emt}/\cos\theta_2)t}, \tag{7}$$

where μ_{inc} $(\mathrm{cm^2\,g^{-1}})$ and μ_{emt} $(\mathrm{cm^2\,g^{-1}})$ are the mass absorption coefficients [19], and t is the mass thickness of the target $(\mathrm{g{\bullet}cm^{-2}})$. The angles of incident photons and emitted x-rays with respect to the normal at the surface of the sample (θ_1 and θ_2) were both equal to $45°$ in the present set-up.

Table 1. K shell fluorescence yields for Ti, V, Cr, Fe, Co, Ni and Cu elements and their halogen compunds.

Compound	Present work	Bambynek [1]	Krause [14]	Hubbell [2]	Durak [7]	Şimşek [3]
^{22}Ti	0.173 ± 0.005	0.219	0.214	0.208		0.214
TiF$_3$	0.182 ± 0.005					
TiF$_4$	0.203 ± 0.006					
^{23}V	0.202 ± 0.006	0.249	0.243	0.249		0.240
VF$_3$	0.106 ± 0.003					
VF$_4$	0.153 ± 0.005					
^{24}Cr	0.221 ± 0.007	0.281	0.275	0.286		0.291
CrF$_2$	0.248 ± 0.007					
CrF$_3$	0.186 ± 0.006					
^{26}Fe	0.270 ± 0.008	0.347	0.340	0.336	0.330	0.331
FeF$_2$	0.132 ± 0.004					
FeF$_3$	0.144 ± 0.004					
FeF$_3 \cdots$ 4H$_2$O	0.192 ± 0.006					
^{27}Co	0.286 ± 0.009	0.381	0.373	0.382		0.355
CoF$_2$	0.290 ± 0.009					
CoF$_3$	0.297 ± 0.009					
CoF$_2 \cdots$ 4H$_2$O	0.293 ± 0.009					
CoCl$_2$	0.279 ± 0.008					
CoCl$_2 \cdots$ 6H$_2$O	0.282 ± 0.005					
^{28}Ni	0.322 ± 0.008	0.414	0.406	0.410	0.412	0.448
NiF$_2$	0.335 ± 0.010					
NiF$_2 \cdots$ 4H$_2$O	0.337 ± 0.010					
NiCl$_2$	0.324 ± 0.010					
NiCl$_2 \cdots$ H$_2$O	0.328 ± 0.010					
NiCl$_2 \cdots$ 6H$_2$O	0.327 ± 0.010					
^{29}Cu	0.350 ± 0.011	0.446	0.440	0.442	0.412	0.455
CuF$_2$	0.359 ± 0.011					
CuF$_2 \cdots$ 3H$_2$O	0.369 ± 0.011					
CuCl	0.344 ± 0.010					
CuCl$_2 \cdots$ 2H$_2$O	0.356 ± 0.011					

4. Results and discussion

The measured K-shell fluorescence yields ω_K are presented in Table 1 and compared with available literature experimental results. The over all errors in the experimental determination of the K_α and K_β XRF cross-sections are estimated as 2.5–3% and are due to counting statistics, background determination, self-absorption correction and $I_0 G \varepsilon$ determination.

Chemical effects on K-shell fluorescence yields ω_K of the element under investigation depend on the chemical environment because of the partially filled 3d subshell of first transition elements. The individual characteristics of the structure of molecules, complexes, and crystals mainly affect the energy position of the K_α line. Actually, an atom in a molecule or crystal differs from the free atom. Participation of the atom in a chemical bond leads to a change in its electron density, and the valence electron density is changed to an especially high degree. This can be described most simply and graphically using the idea of effective charge. The electron density decreases or increases depending on the type of bonding with adjacent atoms in a molecule or crystal. The lattice energy is 2769, 5870, 2878, 5991, 2709, 2845, 6111, 2753, 2774 kj mol^{-1} for FeF$_2$, FeF$_3$, CoF$_2$ CoF$_3$, CoCl$_2$, NiF$_2$, NiF$_3$, NiCl$_2$, CuCl$_2$, respectively . It is clear from these results that the bond lenght in the CoF$_2$, CoCl$_2$ NiF$_2$, NiCl$_2$,CuCl$_2$ are shorter than the bond length in CoF$_3$, NiF$_3$, CuF$_2$ [20].

References

[1] W. Bambynek, B. Crasemann, R. W. Fink, H. U. Freund, H. Mark, C. D. Swift, R. E. Price and P. V. Rao, *Rev. Mod. Phys.*, **44**, (1972)**,** 716.

[2] J. H. Hubbell, P. H. Trehan, N. Singh, B. Chand, D. Mehta, M. L. Garg, R. Garg, S. Singh and S. Puri, *J. Phys. Chem. Ref. Data.*, **23**, (1994), 339.

[3] Ö. Şimşek, O. Doğan, Ü. Turgut and M. Ertuğrul, *Radiat. Phys. Chem.*, **58**, (2002), 207.

[4] E. McGuire, *J. Phys. Rev.*, **185**, (1970),1.

[5] E. McGuire, *J. Phys. Rev. A.*, **24**, (1970), 273.

[6] D. L. Walters and C. P. Bhalla, *Phys. Rev.*, A**3**, (1971), 1919.

[7] R. Durak and Y. Özdemir, *Radiat. Phys. Chem.*, **61**, (2001), 19.

[8] R. Durak, *Physica Scripta*, **58**, (1998), 111.

[9] R. Durak and Y. Şahin, *Phys. Rev. A.*, **57**, (1998), 2578.

[10] Ö. Söğüt, E. Baydaş and E. Büyükkasap, *J. Trace Microprobe Techn.*, **173**, (1999), 285.

[11] Ö. Söğüt, E. Baydaş, E. Büyükkasap, Y. Şahin and A. Küçükönder, *J. Radioanal. Nucl. Chem.*, **25 1**, (2002), 119.

[12] E. Storm, I. Israel, *Nucl. Data Tables.*, **A7**, (1970), 565.

[13] J. H. Scofield, Report UCRL 51326, *Lawrence Livermore Lab., Livermore, CA* (1973)**.**

[14] M. O. Krause, *J. Phys. Chem. Ref. Data.*, **8**, (1979), 307.

[15] J. H. Scofield, *Atom. Data Nucl. Data Tables*, **14**, (1974), 121.

[16] M. L. Garg, S. Kumar, D. Mehta, H. R. Verma , P. C. Mengal and P. N. Trehan, *J. Phys. B: At. Mol. Phys.*, **18**, (1985), 4529.

[17] C. Bhan, S. N. Chaturvedi and N. Nath, *X-Ray Spectrom.*, **15**, (1986), 217.

[18] S. Singh, D. Mehta, M. L. Garg, S. Kumar, N. Singh, P. C. Mangal and P. N. Trehan, *J. Phys. B: At. Mol. Phys.*, **20,** (1987), 3325.

[19] J. H. Hubbell and M. S. Seltzer, *National Institute of Standards and Technology Report No. NISTIR*, (1995), 5632.

[20] R. C. Weast, *Handbook of Chemistry and Physics*, CRC Press. (1985–1986)