CHEMICAL EFFECTS ON THE K_β/K_α INTENSITY RATIOS IN FIRST-ROW TRANSITION ELEMENT COMPOUNDS

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Chemical effects on the K_β/K_α X-ray intensity ratios for some first-row transition element compounds were studied experimentally and calculated. The vacancies in the K shell were created by 59.5 keV γ rays from an ^{241}Am radioactive source and characteristic X-ray radiation from sample was measured by using Si(Li) and Ge(Li) detectors. The calculations were carried out using Brunner's model. The calculated relative K_β/K_α X-ray intensity ratios are in good agreement with the present and the previously published experimental data.

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1. Introduction

The study of the influence of chemical environment on the characteristic X-rays is of great importance for atomic physics and applied research. Therefore, the dependence of relative intensities in X-ray emission spectra on the chemical surroundings of emitted atom and excitation mode has been the subject of extensive experimental and theoretical investigation [1–28].

Earlier results concerned with the chemical environment which affect the K_β/K_α X-ray intensity ratios in coordination compounds of $3d$ elements and some other compounds are summarised in Table I. In compounds the chemical effects are interpreted in terms of valence electron distribution and chemical bonding. In the recent years, we measured the K_β/K_α X-ray intensity ratios for $3d$ elements

TABLE I

Earlier studies on chemical effects.

Compounds	Mode of excitation	Dependence of K_β/K_α	Ref.
3d elements	Electron capture and photoionisation	few percent	[2]
3d elements	PIXE and XRF	up to 5%	[23]
Mn compounds	Photon excitation	up to 10%	[27]
3d elements	Photon excitation	up to 5%	[5]
Ag and Mo	Photon excitation	No deviation as expected for 4d elements	[5]
Fe and Mn	Electron capture and photoionisation	up to 10%	[1]
Ti,Cr,Mn	Electron impact ionisation	up to 6%	[16]
Cr and Mn	Photon excitation	Compounds with T_d symmetry are generally larger than those with O_h symmetry	[8]
3d elements	Photon excitation	up to 9%	[25]
Cr,Mn,Co,Cu	Photon excitation	1–16%	[17]
Ti,V,Fe	Photon excitation	1–12%	[19]
Se,Br,Zr,Ce	Photon excitation	The smallest deviation	[19]
3d elements	Photon excitation	Compounds with T_d symmetry are generally larger than those with O_h symmetry	[18]
Cr,Mn,Fe	Radioactive decay and photon excitation	4%	[20]
Cs,Ba	Radioactive decay and photon excitation	The smallest deviation	[20]
^{51}Cr labelled compounds	Electron capture decay	up to 12%	[4]
^{51}Cr and ^{51}Mn	Electron capture decay	5–10%	[12]
Ti	Electron impact ionisation	4%	[10]
^{51}Cr doped solids	Electron capture decay	Difference between compounds before and after annealing ranging from 2 to 3%	[15]
Cu alloys	Photon excitation	up to 3%	[28]
CrNi and CrAl alloys	Photon excitation	up to 3.5%	[21]

both in pure elements and in various chemical compounds and alloys using a Ge(Li) and Si(Li) detector systems [17–21].

In the reported values of K_β/K_α X-ray intensity ratios of 3d elements and their compounds, the deviations in the results from pure element and from com-

pounds are ranging from 3 to 16%. These deviations were attributed to variations in the number of valence electrons [17], coordination number, and absorption effects of the ligands [18]. Furthermore, we observed that deviations 1–16% for $3d$ elements [19] are much larger than those for high Z elements (1–4%). Moreover, it was found that for first-row transition elements the K_β/K_α X-ray intensity ratio depended on the mode of excitation [20]. Recently, we have measured the K_β/K_α X-ray intensity ratios in different Cr_xNi_{1-x} and Cr_xAl_{1-x} alloys [21] and found that they differed up to 3.5% between alloys with different concentration.

Band et al. [22] carried out the scattered wave $X\alpha$ molecular orbital calculations for some chromium and manganese compounds and evaluated the relative change in the K_β/K_α X-ray intensity ratios. Brunner et al. [23] proposed that the change in the K_β/K_α X-ray intensity ratios was caused by the change in the screening of $3p$ electrons due to delocalization of the $3d$ electrons and estimated the difference between two chemical compounds in a simple model. Mukoyama et al. [24] estimated the chemical effect on the K_{β_2}/K_α ratio for some Tc and Mo compounds using Brunner's model. Furthermore, Raghavaiah et al. [25] calculated relative K_β/K_α X-ray intensity ratios for some $3d$ elements using Brunner's model and compared these with experimental data. The calculated values were found to be consistent with experimental results.

In the present work, K_β/K_α X-ray intensity ratios for some $3d$ elements were measured and calculated by using Brunner's model.

2. Computational method

According to Brunner, $3p$ orbitals suffer a contraction due to the altered screening of $3p$ orbitals by $3d$ orbitals charge delocalization in chemical bonding. The relative K_β/K_α emission rate is given by

$$\frac{\left(\frac{K_\beta}{K_\alpha}\right)_A}{\left(\frac{K_\beta}{K_\alpha}\right)_B} = \frac{1+V_A}{1+V_B}, \tag{1}$$

where $(K_\beta/K_\alpha)_i$ is the K_β/K_α intensity ratio for the i-th chemical compound; V_i is relative deviation described as $V_i = S_z C_{\text{eff}} K_d$. S_z is the sensitivity of $3p$ contraction to a $3d$ charge delocalization [23]. The values of S_z for $3d$ elements were computed by Brunner et al. [23] using the Dirac–Fock–Slater potential. The valence charge difference $C_{\text{eff},i}$ is evaluated from the Pauling electronegativity concept as follows:

$$C_{\text{eff}} = V_f \left\{1 - \exp[-(X_A - X_B)^2/4]\right\}, \tag{2}$$

where V_f is formal oxidation number of the parent atom and X_A and X_B are the Pauling electronegativities [29] for atom A and B forming chemical bonding and K_d is the share of C_{eff}. Brunner et al. used 0.52 for K_d, for the transition elements. The calculated values of K_β/K_α ratios are given in Table II.

TABLE II

Relative K_β/K_α X-ray intensity ratios. ON — oxidation number.

Relative intensity ratios	$\frac{(ON)_1}{(ON)_2}$	$C_{eff,1}/C_{eff,2}$	Present studies		Earlier studies	
			Calc. values	Exp. values	Calc. values	Exp. values
$Mn/KMnO_4$	0/7	0.000/4.424	0.925	–	0.925[25]	0.911[25]
$Mn(NO_3)_2 \cdot H_2O/KMnO_4$	2/7	0.121/4.424	0.927	–	–	0.928[17]
$MnSO_4 \cdot H_2O/KMnO_4$	2/7	0.442/4.424	0.933	–	–	0.920[17]
$Mn(CO_3)/KMnO_4$	2/7	0.442/4.424	0.933	–	–	0.907[17]
$MnBr_2/KMnO_4$	2/7	0.689/4.424	0.937	–	–	0.894[18]
$MnCl_2 \cdot 4H_2O/KMnO_4$	2/7	0.860/4.424	0.939	0.933	–	–
$MnCl_2 \cdot 4H_2O/Mn(NO_3)_3 \cdot 9H_2O$	2/2	0.860/0.121	1.012	1.006	–	–
$MnCl_4/KMnO_4$	4/7	1.720/4.424	0.954	–	–	0.923[18]
$MnO_2/KMnO_4$	4/7	2.528/4.424	0.968	–	0.960[9]	0.973[8]
Fe/FeF_3	0/3	0.000/2.105	0.968	–	–	0.932[19]
FeS/FeF_3	2/3	0.230/2.105	0.971	–	–	0.932[19]
$FeCl_2 \cdot 4H_2O/FeF_3$	2/3	0.604/2.105	0.978	1.009	–	–
$FeSO_4/FeF_3$	2/3	0.442/2.105	0.974	–	–	0.955[19]
$FeCl_2 \cdot 4H_2O/FeSO_4$	2/2	0.604/0.442	1.003	1.056	–	–
$Fe(NO_3)_3 \cdot 9H_2O/FeF_3$	3/3	0.181/2.105	0.970	–	–	1.009[19]
$FeCl_3 \cdot 6H_2O/FeF_3$	3/3	0.906/2.105	0.982	–	–	0.990[19]
Fe_2O_3/FeF_3	3/3	1.543/2.105	0.992	–	–	0.997[17]
Co/CoF_3	0/3	0.000/2.105	0.973	–	–	0.937[17]
$Co(ClO_4)_2 \cdot 6H_2O/CoF_3$	2/3	0.121/2.105	0.974	1.094	–	–
$Co(ClO_4)_2 \cdot 6H_2O/CoCl_2 \cdot 6H_2O$	2/2	0.121/0.604	0.994	1.041	–	–
$Co(NO_3)_2 \cdot 6H_2O/CoF_3$	2/3	0.121/2.105	0.974	–	–	0.991[17]
$CoCl_2 \cdot 6H_2O/CoF_3$	2/3	0.604/2.105	0.980	1.051	–	–
CoO/CoF_3	2/3	1.028/2.105	0.986	–	–	0.975[17]
CoF_2/CoF_3	2/3	0.018/2.105	0.991	–	–	0.970[17]
$Ni/NiSO_4$	0/2	0.000/0.442	0.995	0.984	–	–
$Ni/NiCl_2$	0/2	0.000/0.604	0.993	0.984	–	–
$NiSO_4/NiCl_2$	2/2	0.442/0.604	0.998	1.000	–	–
$Cu/Cu(NO_3)_2 \cdot 3H_2O$	0/2	0.000/0.121	0.998	0.956	–	–
$Cu(CN)/Cu(NO_3)_2 \cdot 3H_2O$	1/2	0.060/0.121	0.999	0.994	–	–
$CuI/Cu(NO_3)_2 \cdot 3H_2O$	1/2	0.086/0.121	0.999	0.962	–	–
$Cu(C_2O_4)/Cu(NO_3)_2 \cdot 3H_2O$	2/2	0.442/0.121	1.002	0.982	–	–
$CuBr_2/Cu(NO_3)_2 \cdot 3H_2O$	2/2	0.366/0.121	1.002	0.979	–	–
$CuCN/CuI$	1/1	0.060/0.086	0.999	1.033	–	–
$Cu(C_2O_4)/CuI$	2/1	0.442/0.086	1.003	1.025	–	–
$CuBr_2/CuI$	2/1	0.366/0.086	1.003	1.018	–	–
$Zn/ZnSO_4$	0/2	0.000/0.442	0.996	0.977	0.996[25]	0.980[25]
$Zn/ZnCl_2$	0/2	0.000/0.774	0.993	0.966	–	–
$ZnSO_4/ZnCl_2$	2/2	0.442/0.774	0.997	0.989	–	–

3. Experimental

The samples are excited by 59.5 keV γ rays from a filtered ^{241}Am radioactive source and X-rays emitted from samples were detected by a Ge(Li) (FWHM = 190 eV at 5.9 keV) and Si(Li) (FWHM = 160 eV at 5.9 keV) detectors coupled to a ND66B multichannel analyser. Two typical spectra of $ZnSO_4$ and $ZnCl_2$ are given in Fig. 1 and Fig. 2. Ni and Zn foil samples were corrected as regards to self-absorption while other samples were subjected to particle size correction since they were in powdered form and the samples were very thin. Powder samples were prepared by using the sample preparation cylindrical cup and rod produced in our research laboratory and supported on the mylar film 50×10^{-4} g $\cdot$ cm^{-2} thickness and 3.4 cm diameter. Detector efficiency corrections were carried on data. The efficiency calibration of the system was made by using reference lines of the known intensity in ^{241}Am, ^{57}Co, ^{137}Cs, and ^{54}Mn standard sources under the same experimental geometric conditions. Therefore the absorption effects of the mylar film and the air in the path of the photons were also eliminated. The background was measured by using the calculation of the mean from ten channels

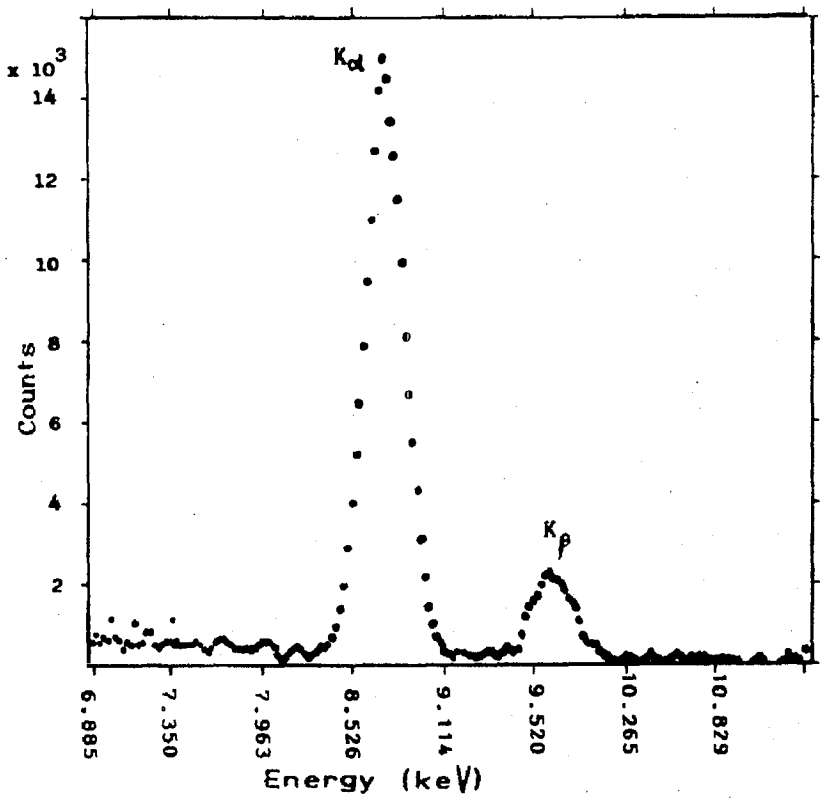

Fig. 1. A typical spectrum of $ZnSO_4$.

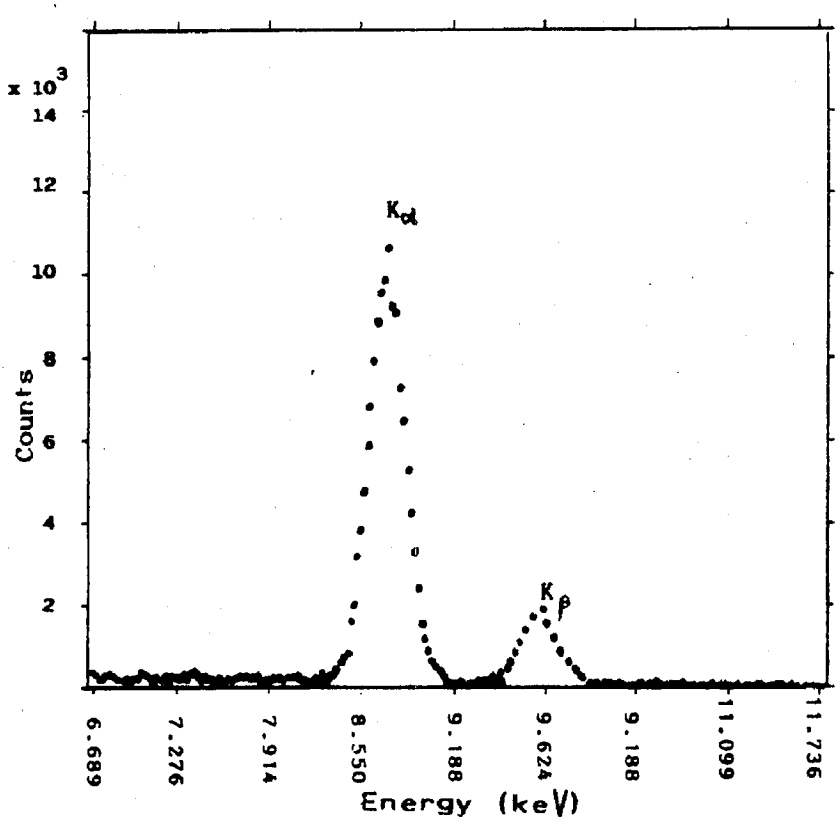

Fig. 2. A typical spectrum of $ZnCl_2$.

except the region about the joining of the K_α and K_β peaks. Sample preparation, experimental method and various correction applied to data have been described more detailed in previous papers [17–21].

4. Results and discussion

The results for the K_β/K_α intensity ratio are presented together with previously published theoretical and experimental results in Table II. Our calculated results are in good compliance with literature data [9, 23]. Our experimental values for Mn compounds $(MnCl_2 \cdot 4H_2O)/KMnO_4$ and $(MnCl_2 \cdot 4H_2O)/[Mn(NO_3)_2 \cdot H_2O]$ are in agreement with calculations. Table II also shows that the calculated K_β/K_α ratios in other manganese compounds agree with earlier experimental studies [8, 9, 17–19] within 4%. The calculated $Mn/(KMnO_4)$ ratio differs from our previous experimental value by $\approx$ 7%. For Fe compounds and $(FeCl_2 \cdot 4H_2O)/(FeF_3)$ ratio, it can be seen that the agreement between calculations and experiment is within 3%. Calculated K_β/K_α intensity ratio for the other compounds of Fe are in agreement with our earlier experimental results [19] within 4%. K_β/K_α ratios calculated for Co compounds agree with present and

our previous experimental results [17] within 12%. From Table II it can be seen that the agreement between calculated values and experiment for Ni is very good and lies within 1%. The experimental K_β/K_α ratios for Cu compounds differ up to 4% and in these compounds difference between calculated value and experimental results lies within 4%. Table II shows that calculated K_β/K_α ratio values of Zn also agree with experimental results. Differences between values of Zn are insignificant. The reason of this may be that the $3d$ shell of Zn is fully occupied and chemical effects are not expected to change relative K_β/K_α intensity ratios of Zn compounds. The insignificant difference between calculations and experiment can be attributed to experimental uncertainties and errors.

The relative K_β/K_α ratios depended on the type of chemical bond, the polarity of the complex or crystal, the coordination number, the ionic character of the chemical bond, and the ligands attached to the emitting atom. In addition, it is clearly evident from the calculated and experimental data that the relative K_β/K_α X-ray intensity ratios vary in accordance to the valence charge difference. This variation depends on the difference of the electronegativities of the bonding atoms and the oxidation number of the related metal atom. It is generally observed that as the ratio of the oxidation number of the related metal atom in one compound to the oxidation number of the related metal atom in another compound $(\text{oxidation number})_1/(\text{oxidation number})_2$ is increased, the relative K_β/K_α X-ray intensity ratios increase as well.

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