A STUDY OF CHEMICAL EFFECTS ON K_β / K_α X-RAY INTENSITY RATIOS IN 3d ELEMENTS

N. VENKATESWARA RAO, S. BHULOKA REDDY, C. V. RAGHAVAIAH,
S. VENKATARATNAM and D. L. SASTRY

Swami Jnanananda Laboratories for Nuclear Research, Andhra University,
Waltair — 530 003, India.

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ABSTRACT — The K_β / K_α X-ray intensity ratios were measured in some pure elements belonging to the 3d shell as well as in their compounds, to look for the influence of the chemical environment on the fluorescence yield ratios. A high resolution Si (Li) detector system was used for the experimental measurements and a low power X-ray generator was used for the excitation. It is found that the K_β / K_α X-ray intensity ratios measured with compounds deviate up to 5 % from the corresponding values of the pure elements. No such deviations are observed for the elements Mo and Ag belonging to the 4d shell.

1 – INTRODUCTION

Brunner et al. [1] have reported that the K_β / K_α X-ray intensity ratio is sensitive to the chemical environment for 3d elements. Their results show deviations up to 4 % between compounds and pure elements. These deviations were attributed to the variations in K_β transition probabilities of valence electrons with change in chemical environment. The same cannot be expected in the case of elements belonging to the N shell, since the K_β transition probability of electrons of this shell is very small. The K shell vacancies in an atom of any element can be caused either via photoelectric effect or through radioactive decay, like K-electron capture or internal conversion of K-electrons. Paić and Pečar [2] have reported different values of the K_β / K_α ratio for elements of the 3d shell following electron capture decay and photon induced excitation. They have attributed this difference in K_β / K_α values to the difference in the mode of excitation. In the above study the chemical environment of the decaying isotope and the one used in the photon induced excitation are not the same. This might be another explanation for the difference in the K_β / K_α values in the two experiments. To confirm this idea, we have studied [3] the dependence on the mode of excitation of the K_β / K_α values using electron capture decaying isotopes and photon induced excitation of natural elements, covering two regions, $Z=20$ to 28 and $Z = 49$ to 82. Our studies reveal dependence of K_β / K_α ratio on the mode of excitation for the 3d shell elements but such a dependence is not found for the high Z elements. Our conclusion is that the apparent small dependence of the K_β / K_α ratio on the mode of excitation is in fact due to different chemical states of the element, consistently with the conclusions of Brunner et al. [1]. If the K_β / K_α ratio dependence on the mode of excitation is possible, then it should manifest itself in the case of high Z elements also, which we have not observed. It is to be noted [4, 5] that the K_{β_5} transition probability is significantly affected by the chemical environment in the case of 3d shell elements, but is not appreciable for the 4d shell elements. The present study concerns a measurement of K_β / K_α X-ray intensity ratios, using a high resolution Si (Li) detector system in some 3d shell and 4d shell elements and their compounds, to look for the chemical effects. The compounds of 3d elements we studied are different from previous ones, and the compounds of 4d elements are studied for the first time in the search for chemical effects. Preliminary results are reported in this paper.

2 — EXPERIMENTAL

The elements Fe, Cu, Zn, Ag and Mo were taken in the form of self supporting foils of thickness ranging from 2 to 3 μm. The chemical compounds $Fe_2(SO_4)_3(NH_4)_2SO_4$, $CuSO_4$, ZnO, $ZnSO_4$, NH_4MoO_3 and Ag_2SO_4 were taken in powdered form and pressed uniformly between two X-ray mylar films of thickness 6 μm. The thickness of these powdered samples was of the order of 250 to 500 μgcm^{-2}.

The present system comprises a high resolution Si (Li) detector (FWHM = 160 eV at 5.9 keV) coupled to a 4K multichannel annalyser with a microprocessor base. The energy calibration of the present system was made in the usual way. The X-ray generator consists of an X-ray tube with Rh target and operates at a maximum power of 25 watts. The tube voltage can be varied from 5 kV to 50 kV and the tube current from 10 to 500 μA. The tube-target-detector geometry is shown in Fig. 1. For the present experiments, the tube was operated at a voltage of 25 kV and a current of 200 μA. Each target of present interest was properly positioned in the sample chamber and excited in order to study the corresponding characteristic X-ray spectrum. The spectra from Fe and its compound are shown in Figs. 2 and 3, respectively. Similar spectra were recorded for the cases of Mo and Ag over a time period of 2 hours each. Since we have used, for excitation of the samples, an X-ray tube which provides high incident flux, the time of collection of data necessary to ensure good

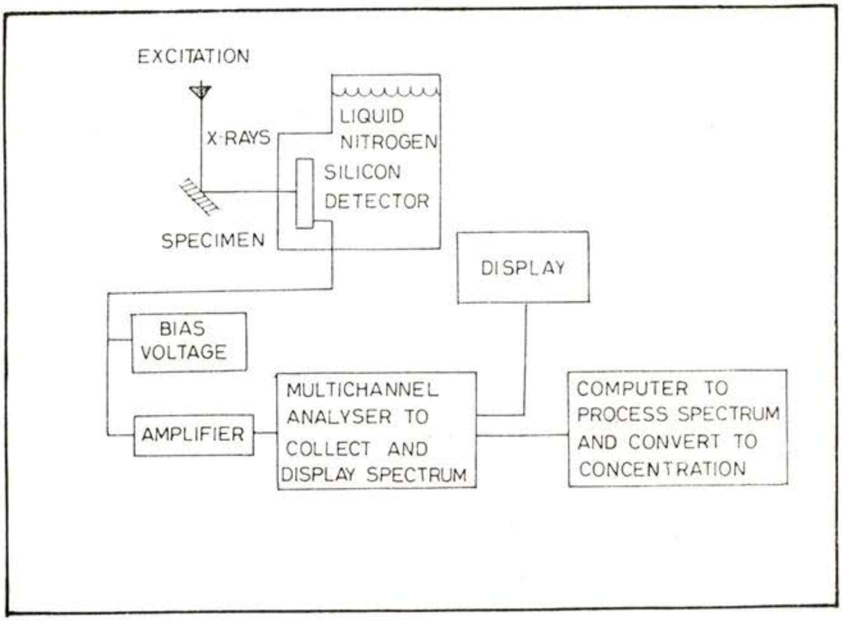
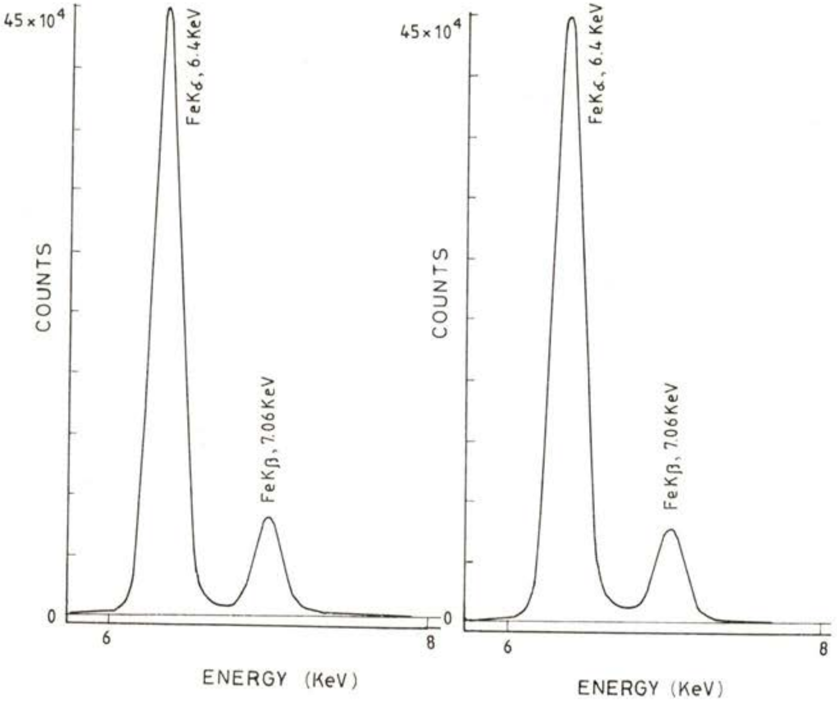


Fig. 1 — Block diagram of the experimental set-up.

statistics is considerably reduced. After defining the background level (assumed to be linear), the K_α and K_β line intensities were determined using the computer as well as by hand. These two methods have yielded consistent intensities in each case. The intensities thus obtained were corrected for self absorption in the target (pure elements), using the usual relationship



Figs. 2 and 3 — Characteristic X-ray spectrum from Fe foil (left) and from $Fe_2(SO_4)_3(NH_4)_2SO_4$ (right).

$$I/I_0 = (1 - e^{-\mu t}) / (\mu t)$$

where μ is the mass absorption coefficient and t the thickness in g cm^{-2}. The relevant absorption coefficients at appropriate X-ray energies were taken from the tables of NBS [6] and UCRL [7]. In the case of compounds the self absorption correction was calculated using the sum rule [8]. The errors that arise in the computation of intensities are mainly due to the efficiency correction. In the present case one considers the ratios of X-ray intensities 'element/compound' eliminating thus the efficiency correction. The errors that arise in the estimate of the intensities are, thus, essentially due to counting statistics and they are less than 0.5 %. The final values of K_α and K_β X-ray intensity ratios were computed and are summarized in Table 1.

3 – RESULTS AND DISCUSSION

The K_α and K_β lines have fine structure which cannot be resolved by our Si (Li) detector system. Thus, the variation in the intensity of the K_{β_5} component due to chemical effects will manifest itself in the present study only in the variation of the total intensity of the K_β components. It is then justifiable to consider the K_β / K_α ratio when studying the effect of the chemical environment, instead of the K_{β_5} / K_α ratio. From Table 1, it can be seen that the K_β / K_α X-ray intensity ratio for the Cu compound deviates from pure Cu by 2.5 % while for Fe it deviates 5 %. Brunner et al. [1] reported values of the K_β / K_α ratio for Fe an Cu compounds which differ from Cu and Fe by 2 % and 1 %, respectively. However, the chemical compounds they used were different. Thus, it may be concluded that the K_β / K_α X-ray intensity ratio depends on the chemical environment for the partially filled 3d shell elements. From Table 1 it may be noted that the K_β / K_α

TABLE 1 — K_β / K_α X-ray intensity ratios for elements and compounds

Element	Compound	$(K_\beta / K_\alpha)_{\text{elem.}} / (K_\beta / K_\alpha)_{\text{comp.}}$
Fe	$Fe_2(SO_4)_3(NH_4)_2SO_4$	0.950 ± 0.011
Cu	$CuSO_4$	0.975 ± 0.010
Zn	ZnO	0.985 ± 0.010
	$ZnSO_4$	0.980 ± 0.010
Mo	NH_4MoO_3	1.000 ± 0.010
Ag	Ag_2SO_4	0.990 ± 0.010

X-ray intensity ratio for Ag and Mo and their corresponding compounds agree with each other within experimental uncertainty. This is ascribed to the fact that the K_β transition probabilities for the 4d electrons are very small.

Further work is in progress to study the dependence of the K_β / K_α ratio on the oxygen content of the compound for each element of the 3d shell.

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