



Effect of chemical environment on K shell emission lines of transition and post transition compounds

Harpreet Singh Kainth

Physics Department, Panjab University Chandigarh, 160014, India



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ABSTRACT

The chemical shift in $K\alpha$ and $K\beta_{1,3}$ X-ray emission lines of ^{47}Ag , ^{48}Cd and ^{50}Sn compounds have been studied by using highly equipped advanced S8 TIGER WDXRF spectrometer. From the results, it is found that halogen compounds are more sensitive for chemical shifts than other compounds. With change of transition probabilities and outermost shell energy levels, chemical shift measured in $K\beta_{1,3}$ X-ray emission lines are observed more than that of $K\alpha$ emission lines. It is also found that chemical shift (ΔE) and effective charge (q) are increased with increasing number of ligands attached to the central metal atom. To show the dependency behaviour of chemical shift and effective charge with each other, we establish a linear relation between them in different ^{48}Cd and ^{50}Sn compounds.

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1. Introduction

X-ray fluorescence (XRF) spectroscopy is an influential tool to study the chemical state analysis in various types of compounds. The chemical behaviour of transition and post transition atoms (especially Ag, Cd and Sn) is determined by the valence nl electrons. It is also well known that when the valence electrons are added or removed from the atom, the wave function and eigenvalues of the inner shell electronic state changes which results in change in the peak energy shift. During the formation of the chemical bond, atom in a metal gets transformed into ions result in positive or negative shifts. These shifts occur due to distortion of atomic energy levels, transfer of electronic charge from cation to anion, as a result of which the core binding energy of the electron changes. The slightly change in binding energy of electron is called chemical shift (ΔE) and is defined as $E_{\text{metal}} - E_{\text{compound}}$, where E_{metal} denotes the central peak position of pure metal and E_{compound} is the central peak position of the relevant compounds [1].

In $K\alpha$ and $K\beta_{1,3}$ X-ray emission lines, spectral changes highly depend on the chemical environment which arise predominantly from the exchange interaction between the core hole. When a 1s electron of metal cation (Ag^+ , Cd^{2+} , Sn^{2+} and Sn^{4+}) is excited, a core hole is created because of extra potential of the core hole, the electrons are transferred from ligands to the nl valence electrons of

the metal cation, as a result the screening effect of the inner shell energy level changes which produce shifts in the emission lines. The spectral changes for $K\alpha$ emission lines are less pronounced than $K\beta_{1,3}$ emission lines. The core hole effect is a well-known problem and various theoretical approaches exist to include the core hole in the calculation of spectra from photoemission, absorption spectroscopy and K fluorescence main line emission. The effective charge is an informative tool to understand the influence of chemical bonding and chemical effects in the various chemical compounds. It is explained in terms of electronegativity scale where more electropositive element loses valence electron charge to the more electronegative element. The electronegativity is the important parameter for the effective charge to determine whether the atom is positively charged or not depending on the neighbouring ligand. Many authors [2–7] reported the physical significance and origin of chemical shift and effective charge in different chemical compounds and correlate with each other.

In recent years, chemical shift becomes more interesting topic for many researchers working in the spectroscopy field. X-ray photoelectron spectroscopy (XPS) and energy dispersive X-ray fluorescence (EDXRF) spectrometers are the most common employed method used to identify the peak shifts in different chemical compounds [8–11]. Numerous studies [12–18] have been undertaken to investigate the possibilities of various chemical properties of transition and non-transition compounds in $K\alpha$ and $K\beta_{1,3}$ X-ray emission lines. However, having limited detector resolution, poor data reliability and weak radioactive lab source used, these types

E-mail address: harpreet.2january@gmail.com

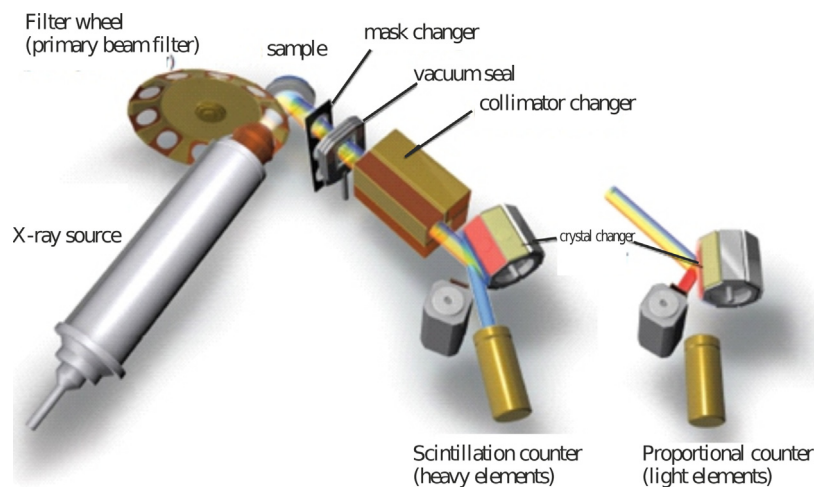


Fig. 1. Schematic diagram of S8 TIGER WDXRF spectrometer.

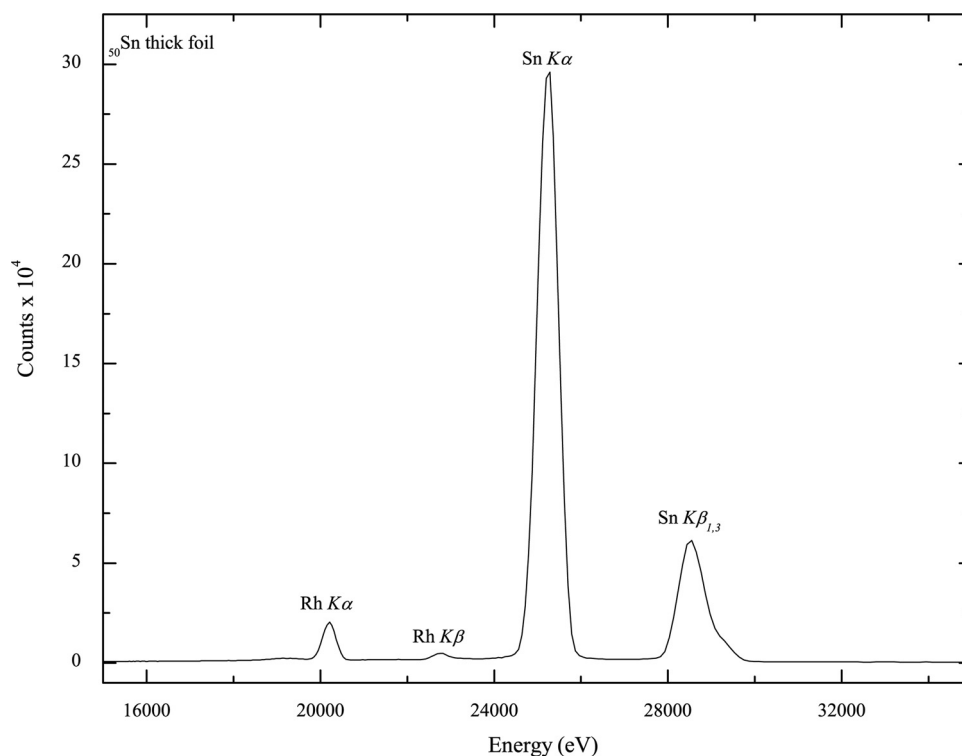


Fig. 2. Represents the $K\alpha$ and $K\beta_{1,3}$ X-ray emission spectra of ^{50}Sn foil.

of spectrometers suffers with lack of stability, electrostatic effects and uncertainty in the emission curves which requires large number of complex corrections. To avoid these types of problems to some extent, wavelength dispersive X-ray (WDXRF) spectrometer with different ranging of high resolution crystals are used. Recently, using WDXRF technique, Baydas et al. [19,20] investigated the effect of chemical environment in oxides form of ^{22}Ti , ^{24}Cr , ^{26}Fe , ^{27}Co and ^{29}Cu compounds in $K\alpha$ and $K\beta_{1,3}$ X-ray emission lines. Moreover, Mokuno et al. [21] proposed a new WD-PIXE spectrometer with high resolution and detector efficiency for chemical state analysis of ^{6}C $K\alpha$, ^{26}Fe and ^{29}Cu $L\alpha$ using a light ion microbeam. Kavčić et al. [22] studied the chemical effect in $K\alpha$ and $K\beta$ emission spectra of different oxidation of ^{16}S in FeS , Na_2SO_3 , Na_2SO_4 , $(\text{NH}_4)_2\text{SO}_4$ samples using wavelength dispersive spectrometer.

In the view point of past studies, different methods have been employed to determine the effective charge but in X-ray emission

lines, chemical effect combination and their relative theoretical explanations on the different chemical compounds have not been established yet completely. In the present work, our main objective is to discuss the role and cause of factors affecting chemical shift. We also find a correlation of effective charge with the chemical shift in given K shell X-ray emission lines of different chemical forms of ^{47}Ag , ^{48}Cd and ^{50}Sn compounds.

2. Experimental details

2.1. Instrumentation

The chemical shift in $K\alpha$ and $K\beta_{1,3}$ X-ray emission lines for different chemical forms of ^{47}Ag , ^{48}Cd and ^{50}Sn elements were measured using WDXRF spectrometer (Model: S8 TIGER, Bruker,

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