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Charge transfer and delocalization studies from $K\beta$-to-$K\alpha$ intensity ratios in Co_xCu_{1-x} alloys

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ABSTRACT

$K\beta$-to-$K\alpha$ X-ray intensity ratios of Co and Cu have been measured in pure metals and in alloys of Co_xCu_{1-x} ($x = 0.8$, 0.7, 0.6, 0.5, 0.4, 0.3 and 0.2) following excitation by 22.69 keV X-rays from a ^{109}Cd radioactive point source. The valence-electronic configurations of these metals were determined by corporation of measured $K\beta$-to-$K\alpha$ X-ray intensity ratios with the results of multiconfiguration Dirac–Fock (MCDF) calculation for various valence-electronic configurations. Valance electronic configurations of Co and Cu in alloys indicate significant differences with respect to the pure metals. Our analysis indicates that these differences arise from delocalization and/or charge transfer phenomena in alloys. Namely the observed change of the valence-electronic configurations of metals in alloys can be explained with the transfer of 3d electrons from one element to the other element and/or the rearrangement of electrons between 3d and 4s, 4p states of individual metal atoms.

1. Introduction

The variety of physical properties of the 3d-transition metals and the large number of applications of these metals and their compounds and alloys create the need for understanding the valence-electronic configurations of 3d-transition metals in various systems. This stimulates the development of experimental and theoretical methods for investigate the influence of chemical/solid state effects on valence electronic structure of 3d-transition metals. The $K\beta$-to-$K\alpha$ X-ray intensity ratios of 3d-transition metals depends on the chemical environment of these metals in their alloys (Bhuinya and Padhi, 1992, 1993; Padhi and Dhal, 1995; Söğüt et al., 1995; Raj et al., 1999a, 2000a, 2001a; Pawłowski et al., 2002; Söğüt, 2006; Han and Demir, 2009) and compounds (Brunner et al., 1982; Arndt et al., 1982; Mukoyama et al., 1986; Küçükönder et al., 1993; Padhi et al., 1993; Chang et al., 1993, 1994; Kawai et al., 1994; Raj et al., 1998a,b, 1999b,c, 2000b, 2001b). This dependence can be explained as the result of the changes of the 3d electron population of the transition metal because of chemical/solid state effects, which modify 3p orbital more than 2p orbital resulting in a change in the $K\beta$-to-$K\alpha$ X-ray intensity ratio of the metal. Thus the $K\beta$-to-$K\alpha$ X-ray intensity ratio becomes a sensitive tool to study the valence-electronic configurations of the 3d-transition metals in various systems.

Comparison of the experimental $K\beta$-to-$K\alpha$ X-ray intensity ratio values with the theoretical values obtained from the multiconfiguration Dirac–Fock (MCDF) calculations for various valence-electronic configurations is a convenient method for determining the valence-electronic configurations of the 3d-transition metals in alloys and compounds. This method was worked out and tested for the valence-electronic configuration of various 3d-transition metals in some earlier works (Polasik, 1998; Mukoyama et al., 2000; Raj et al., 2002). The MCDF method has been mainly developed by Grant and co-workers and is described in detail (Grant, 1970, 1974, 1984; Grant et al., 1980; Grant and McKenzie, 1980; McKenzie et al., 1980; Hata and Grant, 1983; Dyall et al., 1989).

The present experimental study is on the valence-electronic configuration of Co and Cu in alloys from $K\beta$-to-$K\alpha$ X-ray intensity ratios and has two-sided aspect. The main goal of this study is related to the estimation (by the comparison of the experimental $K\beta$-to-$K\alpha$ X-ray intensity ratio values with the theoretical ones obtained MCDF calculations) of the numbers of 3d, and 4s, 4p electrons for Co_xCu_{1-x} alloys. In this way the valence electronic structure obtained for a given metal in an alloy is found to be different from that of pure metal. This difference was explained with the charge transfer and electron rearrangement processes. Results of this part show that $K\beta$-to-$K\alpha$ X-ray intensity ratios are a useful and sensitive physical quantity to determine the valence-electronic configurations of the 3d-transition metals.

The second aim of this study is to estimate the average number of 3d, and 4s, 4p electrons for an alloy. The average valence-electronic configuration of an alloy obtained in this way differs from

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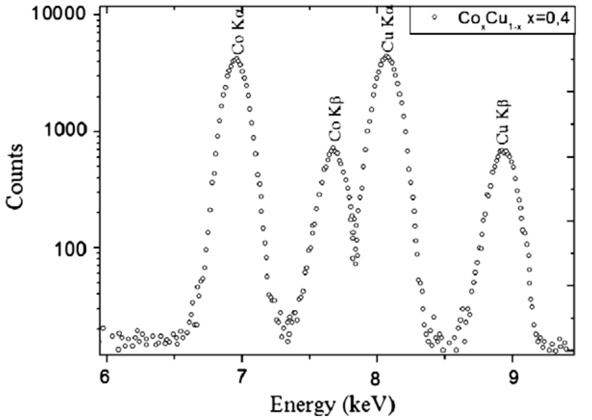

Fig. 1. A typical *K* X-ray spectrum of $Co_{0.4}Cu_{0.6}$ alloy obtained by 22.69 keV X-ray.

superposition of the configuration of pure metals constituting this alloy. This originates from the changes of valence-electronic configuration of individual metals in alloys.

2. Experimental details, data analysis and corrections

The measurements were carried out using high purity alloys (in powder form). The powder material is pelletized into the size of 13 mm diameter. The samples were irradiated using 22.69 keV X-rays from a 10 mCi ^{109}Cd radioactive point source. For each sample, emitted X-rays were detected by a Si(Li) detector (full width at half maximum = 160 eV for a 5.9 keV X-ray peak, active area of 12 mm^2, thickness of 3 mm, and Be window thickness of 0.025 mm) coupled with a multichannel analyzer system and spectroscopy amplifier. The detector was also placed in a step-down shield made from Pb, Fe, and Al to minimize the detection of any radiation coming directly from the source and scattered from the surroundings.

A typical K X-ray spectrum of $Co_{0.4}Cu_{0.6}$ alloy is shown in Fig. 1. All the X-ray spectra were carefully analyzed by means of the Microcal Origin 7.5 Demo Version software program using a multi-Gaussian least-square fit method in order to determine the net peak. The $K\beta$-to-$K\alpha$ intensity ratios were determined from peak areas fitted to Gaussian function after applying necessary corrections to the data. For measured ratios corrections are needed because of the difference in the $K\alpha$ and $K\beta$ self-attenuations in the sample, difference in the efficiency of the Si(Li) detector and air on the path between the sample and the Si(Li) detector window.

The $I_{K\beta}/I_{K\alpha}$ intensity ratio is obtained from the following equation (Han et al., 2007a,b);

$$\frac{I_{K\beta}}{I_{K\alpha}} = \frac{N_{K\beta}}{N_{K\alpha}}\frac{\beta_{K\alpha}}{\beta_{K\beta}}\frac{\varepsilon_{K\alpha}}{\varepsilon_{K\beta}} \quad (1)$$

where $N_{K\alpha}$ and $N_{K\beta}$ represent the counts under the $K\alpha$ and $K\beta$ peaks, $\beta_{K\alpha}$ and $\beta_{K\beta}$ are the self-absorption correction factors of the target for both the incident and emitted photons, and $\varepsilon_{K\alpha}$ and $\varepsilon_{K\beta}$ are the detector-efficiency values for the $K\alpha$ and $K\beta$ X-rays, respectively.

The self-absorption correction factor β, for the incident photons and emitted K X-ray photons and is given by:

$$\beta = \frac{1 - \exp\left[-((\mu/\rho)_i/\cos\theta_1 + (\mu/\rho)_e/\cos\theta_2)t\right]}{((\mu/\rho)_i/\cos\theta_1 + (\mu/\rho)_e/\cos\theta_2)t} \quad (2)$$

where $(\mu/\rho)_i$ and $(\mu/\rho)_e$ are the mass attenuation coefficients (cm^2/g) of incident photons and emitted characteristic X-rays, respectively. θ_1 and θ_2 are the angles of incident photons and emitted X-rays with respect to the normal at the surface of the sample in the present setup and t is the mass thickness of the sample in g/cm^2. To estimate the self-absorption correction in the sample and the absorption correction in the air path we used the mass attenuation coefficients obtained by means of a computer program named WinXcom (Gerward et al., 2004). This program uses mixture rule to calculate the partial and total mass attenuation coefficients for all elements, compounds and mixtures at standard as well as selected energies.

The mass attenuation coefficients $(\mu/\rho)_C$ for any chemical compound or mixture are estimated using the elemental values in the following Bragg's-rule formula (Jackson and Hawkes, 1981).

$$(\mu/\rho)_C = \sum_i w_i(\mu/\rho)_i \quad (3)$$

where w_i is the proportion by weight of the ith constituent and $(\mu/\rho)_i$ is the mass attenuation coefficient for the ith constituent in the compound.

The experimental K_i X-ray fluorescence cross-sections were evaluated using the relation:

$$\sigma_{Ki} = \frac{N_{Ki}}{I_0 G \varepsilon_{Ki} \beta t} \quad (i = \alpha, \beta) \quad (4)$$

where N_{Ki} is the net number of counts under the corresponding photopeak, ε values at various energies were obtained from the variation of the factor $I_0G\varepsilon$ with energy, where I_0 is the intensity of the incident radiation and G is the geometrical factor dependent on the source-sample geometry.

Table 1
$K\beta$-to-$K\alpha$ X-ray intensity ratios of Co and Cu in pure metals and different alloys ($(I_{K\beta}/I_{K\alpha})_A$: experimental $K\beta$-to-$K\alpha$ X-ray intensity ratios and $(I_{K\beta}/I_{K\alpha})_B$: relative $K\beta$-to-$K\alpha$ X-ray intensity ratios with respect to the pure metals).

Sample	Co		Cu		$I_{K\beta}/I_{K\alpha}$ from previous study	
	$(I_{K\beta}/I_{K\alpha})_A$	$(I_{K\beta}/I_{K\alpha})_B$	$(I_{K\beta}/I_{K\alpha})_A$	$(I_{K\beta}/I_{K\alpha})_B$		
Pure Co	0.1342 ± 0.0063	1.0000	–	–	0.1335[a,b]	0.1350[d]
$Co_{0.8}Cu_{0.2}$	0.1304 ± 0.0066	0.9718	0.1345 ± 0.0181	0.9821		
$Co_{0.7}Cu_{0.3}$	0.1307 ± 0.0069	0.9743	0.1349 ± 0.0141	0.9846		
$Co_{0.6}Cu_{0.4}$	0.1308 ± 0.0073	0.9746	0.1378 ± 0.0117	1.0061		
$Co_{0.5}Cu_{0.5}$	0.1318 ± 0.0082	0.9822	0.1396 ± 0.0103	1.0193		
$Co_{0.4}Cu_{0.6}$	0.1330 ± 0.0090	0.9914	0.1408 ± 0.0090	1.0277		
$Co_{0.3}Cu_{0.7}$	0.1343 ± 0.0104	1.0008	0.1416 ± 0.0080	1.0339		
$Co_{0.2}Cu_{0.8}$	0.1348 ± 0.0121	1.0042	0.1435 ± 0.0069	1.0476		
Pure Cu	–	–	0.1370 ± 0.0052	1.0000	0.1360[c]	0.1370[d]

[a] Raj et al. (2002).
[b] Pawłowski et al. (2002).
[c] Raj et al. (1998b).
[d] Khan and Karimi (1980).