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Relative K x-ray intensities in some selected elements between Mn and Sb following ionization by 59.54-keV γ rays

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A systematic study of relative K x-ray intensities has been made on the elements Mn, Ni, Cu, Ga, Ge, Ag, Cd, Sn, and Sb in the form of pure elements, alloys, and compounds to look into the influence of solid-state effects. The vacancies in the K shell were created by 59.54-keV γ rays from an ^{241}Am radioactive source and the x rays were measured using a Si(Li) detector. Our results are in good agreement with the previously published data. Alloying was found to have a negligible effect on the $K\beta$-to-$K\alpha$ ratio. The present experimental data agree very well with Scofield's [At. Data Nucl. Data Tables **14**, 121 (1974)], theoretical data in all cases except silver and antimony.

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I. INTRODUCTION

A precise measurement of the $K\beta$-to-$K\alpha$ intensity ratio is of great interest to quantitative analysis of trace elements. Several recent studies [1–10] point to the continued interest in the measurement of the $K\beta$-to-$K\alpha$ ratio. In these measurements the K-shell vacancies were created either by internal conversion or by several types of projectiles—photons [4–6], electrons [7], protons [8–10], or heavier ions [11,12]—and filled by outer electrons leading to the emission of K x rays. The measured values have been compared with theoretical results for free atoms. Good agreement has been achieved with the relativistic calculations of Scofield [13], which takes into account the overlap and exchange effects. Several studies, theoretical [14,15] as well as experimental [3,16–19] have been reported on the influence of solid-state or chemical effects on the $K\beta$-to-$K\alpha$ ratio. Brunner *et al.* [3] explained their experimental results on $3d$ elements by the change in the screening of $3p$ electrons by a varying $3d$ electron delocalization as well as the polarization effect.

Although the $K\beta$-to-$K\alpha$ ratio seems to be an easily measurable quantity, the experimental data from individual experiments still present a relatively large spread, and even the average experimental data presented by the two compilations of these data [20,21] differ by as much as 3%. Several factors contribute to this spread, such as the method of vacancy production, target chemical effects, etc. Other possible relevant sources of error are the eventual use of low-resolution detectors, data analysis procedures to obtain the areas under the peaks, and the uncertainty of the various corrections involved such as detector efficiency and self-absorption in the target.

The measurements reported here were made in the medium-Z region using a Si (Li) detector, and the areas under the peaks have been carefully determined by the method of least squares by Silin [22]. The $K\beta$-to-$K\alpha$ intensity ratios were measured for Mn, Ni, Cu, Ga, Ge, Ag, Cd, Sn, and Sb, the K-shell vacancies being created by 59.54-keV γ rays from an ^{241}Am point source.

II. EXPERIMENTAL TECHNIQUE

A commercial radioactive ^{241}Am source was used, with an activity of 200 mCi. The experimental arrangement was discussed in detail in our previous paper [16]. The 59.54-keV γ rays from the source are collimated and directed to impact on the target at an angle of 70° to the normal of the target surface. The fluorescent x rays emitted from the target are detected with a 30-mm^2 area and 5-mm-thick Si (Li) detector kept at 90° to the target face.

III. DATA ANALYSIS

A fit to the experimental data was achieved in each case by representing the $K\alpha$ and $K\beta$ peak shapes with Gaussian functions, allowing the widths, means, and areas of the calculated peaks, and three parameters specifying a quadratic background all to vary in combination until an optimized set was obtained by the method of least squares. Figure 1 shows a typical experimental spectrum of Ag.

Sources of error contributing to the uncertainty in the measured $K\beta$-to-$K\alpha$ ratios come mainly from the

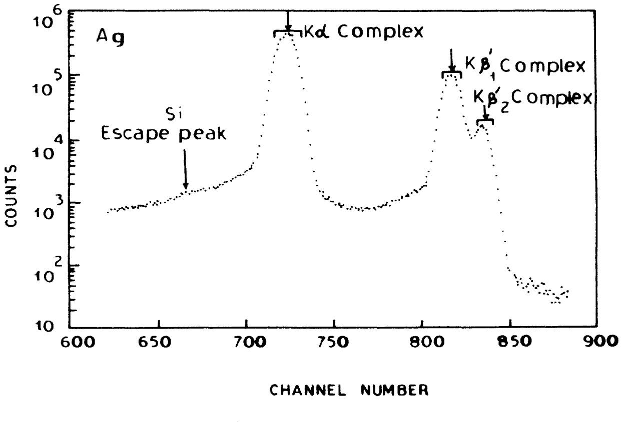

FIG. 1. A typical K x-ray spectrum for Ag.

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difference in the $K\alpha$ and $K\beta$ self-attenuations, air absorption, efficiency correction of the detector, and the statistical error in the total counts collected under each peak. The efficiency of the Si (Li) detector was theoretically calculated using the following expression:

$$\epsilon_d(E)=e^{-(\mu_{\mathrm{Be}}x_{\mathrm{Be}}+\mu_{\mathrm{Au}}x_{\mathrm{Au}}+\mu_{\mathrm{Si}}\Delta x_{\mathrm{Si}})}(1-e^{-\mu_{\mathrm{Si}}x_{\mathrm{Si}}})\ , \tag{1}$$

where μ's are the absorption coefficients due to the Be window of the detector, the gold layer on the Si (Li) crystal, and Si (Li) crystal at the x-ray energy E. Δx_{Si} is the thickness of the insensitive region of the Si (Li) crystal, and x_{Be}, x_{Au}, and x_{Si} are thicknesses of the Be window, the Au layer on the Si (Li) crystal, and the sensitive region of the Si (Li) crystal, respectively. The absorption coefficients are taken from the tables of Hubbell *et al.* [23]. For the present studies the relative efficiency correction on the $K\beta$-to-$K\alpha$ ratio was found to vary from about 1% for low-Z elements to about 14% in the case of Sb. Corrections due to target self-absorption are given by

$$\frac{A_\beta}{A_\alpha}=\frac{\dfrac{\mu_\beta+(\mu_1/\cos\theta)}{\mu_\alpha+(\mu_1/\cos\theta)}\left\{1-\exp\left[-\left[\dfrac{\mu_\alpha+(\mu_1/\cos\theta)}{\rho}\right]\rho x\right]\right\}}{1-\exp\left[-\left[\dfrac{\mu_\beta+(\mu_1/\cos\theta)}{\rho}\right]\rho x\right]}\ , \tag{2}$$

where μ_1, μ_α, and μ_β are the target absorption coefficients for the incident γ rays and the emitted $K\alpha$ and $K\beta$ x rays, and θ is the angle subtended by the incident γ ray with the normal to the target surface. For thick samples $(x \gg 1/\mu)$,

$$\frac{A_\beta}{A_\alpha}=\frac{\mu_\beta+(\mu_1/\cos\theta)}{\mu_\alpha+(\mu_1/\cos\theta)}\ . \tag{3}$$

The above simplification avoids the error introduced in the measured $K\beta$-to-$K\alpha$ ratio due to the target thickness determination. For alloys and compounds the absorption coefficients used are obtained by following Bragg's rule for the addition of absorption coefficients of constituent elements. The errors in the self-absorption correction and air absorption come mainly from the uncertainties in the absorption coefficient data. The expression for the corrected $K\beta$-to-$K\alpha$ ratio is given by

$$\left[\frac{K\beta}{K\alpha}\right]_{\text{corrected}}=\left[\frac{K\beta}{K\alpha}\right]_{\text{measured}}\left[\frac{A_\beta}{A_\alpha}\right]\left[\frac{T_\alpha}{T_\beta}\right]\left[\frac{\epsilon_d^\alpha}{\epsilon_d^\beta}\right]\ , \tag{4}$$

where (T_α/T_β) corresponds to the absorption correction for air column between the target and the Si (Li) detector, and ϵ_d^α and ϵ_d^β are the detector efficiencies for the $K\alpha$ and $K\beta$ x rays, respectively. The correction factors for self-absorption, air absorption, and detector efficiency and their uncertainties are given in Table I. In the present

TABLE I. Correction factors for self-absorption, air absorption, and detector efficiency and their uncertainties.

Element Z	Sample	$\dfrac{A_\beta}{A_\alpha}$	$\Delta\left[\dfrac{A_\beta}{A_\alpha}\right]$	$\dfrac{T_\alpha}{T_\beta}$	$\Delta\left[\dfrac{T_\alpha}{T_\beta}\right]$	$\dfrac{\epsilon_d^\alpha}{\epsilon_d^\beta}$	$\Delta\left[\dfrac{\epsilon_d^\alpha}{\epsilon_d^\beta}\right]$
Mn 25	$\mathrm{Mn_{88}Ni_{12}}$	0.767	0.0153	0.977	0.001	0.996	0.001
Ni 28	$\mathrm{Mn_{88}Ni_{12}}$	0.772	0.0154	0.988	0.001	0.998	0.001
Cu 29	$\mathrm{Cu_{98}Be_2}$	0.770	0.0154	0.998	0.001	0.991	0.001
	$\mathrm{Cu_{29}Ag_{71}}$	0.773	0.0155				
	$\mathrm{Cu_{94}Sn_6}$	0.777	0.0155				
Ga 31	GaSb	0.764	0.0153	0.998	0.001	0.995	0.001
Ge 32	$\mathrm{Ge_{54}Al_{46}}$	0.969	0.0194	0.995	0.001	0.999	0.001
Ag 47	Ag	0.864	0.0173	0.996	0.001	1.044	0.001
		0.845	0.0169	0.995	0.001	1.054	0.001
Ag 47	$\mathrm{Cu_{29}Ag_{71}}$	0.908	0.0182				
		0.896	0.0179				
Cd 48	Cd	0.929	0.0186	0.996	0.001	1.057	0.001
		0.920	0.0184	0.995	0.001	1.072	0.001
Sn 50	Sn	0.945	0.0189	0.997	0.001	1.090	0.001
		0.937	0.0187	0.996	0.001	1.110	0.001
	$\mathrm{Cu_{94}Sn_6}$	0.845	0.0171				
		0.834	0.0167				
Sb 51	GaSb	0.884	0.0177	0.999	0.001	1.127	0.001
		0.874	0.0172	0.999	0.001	1.145	0.001

TABLE II. $K\beta$-to-$K\alpha$ x-ray intensity ratios of some selected elements with atomic number $25 \leq Z \leq 51$ following ionization by 60-keV γ rays. The errors quoted are statistical only.

Element Z	Sample	Sample thickness of present work (mm)	Present expt.	Previous expt.	Theo. result[a]
Mn 25	Pure Mn			0.1385±0.001[b] 0.1219[c] 0.129[d] 0.134[e] 0.135[f] Av.0.132	0.1385
	$Mn_{88}Ni_{12}$	0.5	0.135±0.002		
Ni 28	Pure Ni			0.1363±0.002[g] 0.1328[c] 0.1385±0.0011[j] 0.1349[i] 0.1437[e] Av.0.137	0.1401
	$Mn_{88}Ni_{12}$	0.5	0.142±0.002		
Cu 29	Pure Cu			0.136±0.001[b] 0.1339[c] 0.1382[h] 0.138±0.0011[j] 0.133[d] 0.137[e] 0.136[f] Av.0.136	0.1379
	$Cu_{98}Be_2$	0.5	0.1347±0.0005		
	$Cu_{29}Ag_{71}$	0.5	0.1391±0.0007		
	$Cu_{94}Sn_6$	0.25	0.1351±0.0006		
			Av.0.137±0.001		
Ga 31	Pure Ga			0.137[c] 0.143[f] Av.0.140	
	GaSb	2.0	0.1412±0.0007		
Ge 32	Pure Ge			0.1395[c] 0.1492±0.012[j] 0.1479[i] 0.152[f]	0.1504
	$Ge_{54}Al_{46}$	0.5	0.1528±0.0013		
Ag 47	Pure Ag	0.72	0.2009±0.0003	0.211±0.004[c] 0.203[d] 0.212[e] 0.211[f] Av.0.209	0.213
	$Cu_{29}+Ag_{71}$	0.05	0.2021±0.0004		
Cd 48	Pure Cd	0.06	0.2141±0.0009	0.2155±0.0012[c] 0.2141[h] 0.210[d] 0.216[e] 0.211[f] Av.0.213	0.216
Sn 50	Pure Sn	0.06	0.2183±0.0006	0.2226[c] 0.215[d] 0.222[e] 0.220[f] Av.0.220	0.223
	$Cu_{94}Sn_6$	0.25	0.2223±0.0007		
Sb 51	Pure Sb			0.2254[c]	0.2266
	GaSb	2.0	0.2514±0.0003		

[a] Scofield, Ref. [13].

[b] Bhuinya and Padhi, Ref. [17].

[c] Hansen, Freund, and Fink, Ref. [25].

[d] Coelho, Gaspar, and Eichler, Ref. [24].

[e] Khan and Karimi, Ref. [20]

[f] Salem, Panossian, and Krause, Ref. [21].

[g] Bhuinya and Padhi, Ref. [16].

[h] Casnati *et al.*, Ref. [4].

[i] Rao, Chen, and Crasemann, Ref. [27].

[j] Silvinsky and Ebert, Ref. [26].

measurement the statistical error is found to vary from 0.12% to 1.5%.

IV. RESULTS AND DISCUSSION

The results for the $K\beta$-to-$K\alpha$ ratio are presented in Table II together with the previously published experimental results and the theoretical results of Scofield [13]. For the elements studied here the present results are in good agreement with the most probable experimental results of Khan and Karimi [20] and Salem, Panossian, and Krause [21] except for silver and antimony. Our silver result, however, agrees very well with the recent result of Coelho, Gaspar, and Eichler [24]. The theoretical result of Scofield [13] for silver is about 5% higher than the present result. For Sb we obtain an enhancement of about 10% in the $K\beta$-to-$K\alpha$ ratio over the theoretical value of Scofield [13]. This enhancement may be attributed to the solid-state or chemical effects. The study was made on a thick single crystal sample of GaSb. GaSb is a compound semiconductor which is partly ionic and partly covalent. The change in the electronic structure of antimony in the semiconductor solid has to be taken into account in the theoretical calculation. We hope the present work will stimulate fresh theoretical calculations. Previous data on $K\beta$-to-$K\alpha$ ratios of Mn, Ni, and Cu had a large spread, but the present results for these elements are in close agreement with the most probable results of Khan and Karimi [20] and Salem, Panossian, and Krause [21], and the theoretical results of Scofield [13]. The recent results of Coelho, Gaspar, and Eichler [24] for Mn and Cu are found to be about 3% lower than our present results. The present germanium result is in good agreement with the theoretical result of Scofield [13] and the previously published most probable experimental result [21]. The $K\beta_2'$-to-$K\beta_1'$ ratios of Ag, Cd, Sn, and Sb as given in Table III are in excellent agreement with Scofield's theory [13].

TABLE III. $K\beta_2'$-to-$K\beta_1'$ x-ray intensity ratios of Ag, Cd, Sn, and Sb following ionization by 60-keV γ rays. The errors quoted are statistical only.

Element Z	Sample	Sample thickness (mm)	Present expt. data	Theoretical result [13]
Ag 47	Pure Ag	0.72	0.1752±0.0006	0.1744
	$Cu_{29}Ag_{71}$	0.05	0.1743±0.0006	
			Av. 0.1747±0.0008	
Cd 48	Pure Cd	0.06	0.1796±0.0006	0.1790
Sn 50	Pure Sn	0.06	0.191±0.001	0.1974
	$Cu_{94}Sn_6$	0.25	0.2041±0.0017	
			Av. 0.1975±0.0018	
Sb 51	Pure Sb			0.207
	GaSb	2.0	0.2075±0.0004	

In conclusion we would like to say that the present results for the $K\beta$-to-$K\alpha$ ratio do not confirm the discrepancy between theory and experimental data quoted by Coelho, Gaspar, and Eichler [24] except for silver. In almost all cases we do not see any alloying effect on the $K\beta$-to-$K\alpha$ ratio. This may be because transitions involved in elements such as Ag and Sn originate from the shells far away from the valence orbitals and hence are not influenced due to alloying. For Mn, Ni, and Cu alloys, changes in $3d$-electron population could have altered the $K\beta$-to-$K\alpha$ ratio of these elements from the free-atom values, but as no change has been seen in the present data, this suggests that no appreciable $3d$-electron transfer or delocalization is taking place in the alloy compositions concerned.

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