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Kβ/Kα Intensity Ratios for Elements of Atomic Number 20 to 30

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Abstract

Twenty-five new measurements of Kβ/Kα X-ray intensity ratios for elements in the atomic number range 20 to 30 confirm other recent evidence that the variation with atomic number in this region is much less than previously thought, but there is still some disagreement for atomic numbers above 27. A table of recommended values is given.

Introduction

The relative intensities of Kβ and Kα peaks is of interest for calculating fluorescence corrections in electron microprobe analysis, and for estimating the amount of overlap between the Kβ and Kα peaks of elements adjacent in atomic number. Experimental values of the β/α ratio can also be used to test theoretical atomic models, from which transition probabilities may be calculated.

Until recently it was thought that the β/α ratio decreased rapidly with decreasing atomic number in the range 20 to 30. For example, 'best fit' values given by Nelson and Saunders[1] show a factor of two decrease over this range. However, at that time there were no reliable data for $Z < 24$, and more recent measurements[2,3] have indicated much higher values in this region. We have made measurements using electron-excited spectra of elements from $Z = 20$ to 30 which confirm this observation. However, there is some disagreement among recent measurements for $Z > 27$.

Experimental

The samples used are pure elements and compounds of known composition. The spectra were generated by electrons of 15 or 20 keV energy in an Applied Research Laboratories Inc. (ARL) EMX electron microprobe, with normal electron incidence and 52°30′ X-ray take-off angle, and a Technisch Physische Dienst (TPD) instrument, with 45° electron incidence and X-ray take-off.[4] The spectra were recorded with an Ortec Si(Li) detector (160 eV FWHM at 5.9 keV).

Calculation of the β/α ratio

Background was subtracted by interpolating from below the Kα peak to above the Kβ peak, using Kramers' expression for the continuum, with allowance for absorption.[5] This takes account of the K absorption edge under the Kβ peak, which might otherwise cause significant errors.

The peak areas were determined by a least squares gaussian fit, which was repeated for different numbers of channels to check consistency. For $Z > 27$ it was found that the peak area was significantly dependent on the number of channels, indicating a non-gaussian shape presumably caused by the minor Kβ lines. For these elements the peak areas were therefore obtained by summation between the first channels significantly above background on each side of the peak. The β/α ratios were corrected for the slight difference in absorption between the two peaks. The correction factors were between 0.98 and 1.00 in all cases.

Results

The results are given in Table 1. The accuracy is mainly governed by the background correction for the

Table 1. Experimental values of β/α ratio

Z	Sample	Instr.	kV	β/α	Mean
20	$CaSiO_3$	TPD	20	0.129	
	$CaAl_2O_4$	TPD	20	0.129	
	$Ca_2P_2O_7$	TPD	20	0.131	0.129_7
22	Ti	TPD	20	0.131	
	Ti	ARL	15	0.130	
	Ti	ARL	20	0.129	0.130_0
23	V	TPD	20	0.134	
	V	ARL	15	0.132	
	V	ARL	20	0.132	0.132_7
24	Cr	TPD	20	0.134	
	Cr	ARL	20	0.133	
	Cr_2O_3	TPD	15	0.134	
	Cr_2O_3	TPD	20	0.135	
	Cr_2O_3	ARL	15	0.133	0.133_8
25	Mn	ARL	20	0.135	0.135
26	Fe	TPD	15	0.136	
	Fe	TPD	20	0.137	
	Fe	ARL	20	0.137	
	FeS	TPD	15	0.136	
	FeS	TPD	20	0.135	0.136_1
27	Co	ARL	20	0.138	0.138
28	Ni	TPD	20	0.139	0.139
29	Cu	TPD	20	0.141	0.141
30	Zn	TPD	20	0.143	
	ZnS	TPD	20	0.143	0.143_0

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Table 2. Recommended values of β/α ratio

Z	β/α
20	0.129_3
21	0.130_5
22	0.131_7
23	0.132_8
24	0.134_0
25	0.135_2
26	0.136_3
27	0.137_5
28	0.139_0
29	0.140_6
30	0.142_3

Kβ peak and is estimated to be ± 2%. Variations with instrumental geometry and accelerating voltage are within the experimental error. No significant chemical differences are observed. Mean values for each element are given in Table 1. Recommended values are given in Table 2.

Discussion

Figure 1 compares our results with two other sets of recent measurements. Our results agree with those of Slivinsky and Ebert[3] for all Z, within the experimental error, but differ significantly from those of Salem *et al.*[2] – notably for $Z > 27$. However, all of these measurements do indicate higher β/α values for the lower atomic numbers than had been found in earlier work.[1] Slivinsky and Ebert used a Si(Li) detector, with thin samples excited by X-ray fluorescence. Salem *et al.* also used fluorescence excitation, but their samples were thick, necessitating a correction for self absorption, which was calculated by an approximate method. Furthermore, they used a diffracting crystal spectrometer, and argued that the reflectivity of the crystal was nearly independent of wavelength and that, therefore, no correction was required for this factor. The validity of this assumption is uncertain. We therefore think that the values given by Slivinsky and Ebert are preferable and have compiled a list of recommended values (Table 2) based on a curve (Fig. 1) drawn through their data and ours.

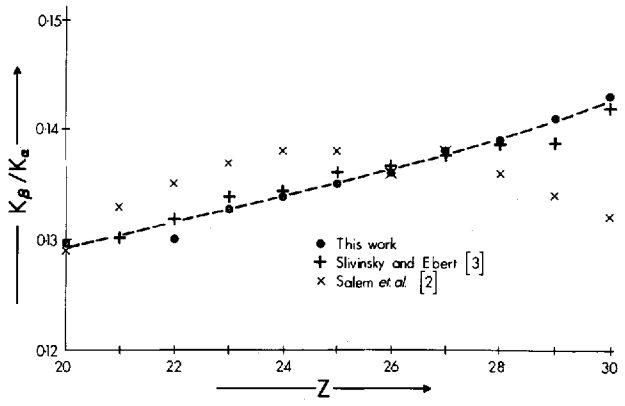

Fig. 1. Kβ/Kα intensity ratios for elements of atomic number 20 to 30.

For the limited range of materials investigated, no significant variations were observed in the β/α ratios for a particular element in the metal or in its different compounds. This might be anticipated from the fact that in the atomic number range 20 to 30, none of the transitions producing the Kβ and Kα peaks involves the valence band. Such variations are likely to become apparent and progressively more important in ratios obtained from elements with $Z < 19$.

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