

$K\beta/K\alpha$ X-RAY INTENSITY RATIO STUDIES ON THE VALENCE ELECTRONIC STATES OF $3d$ -TRANSITION METALS IN SOME OF THEIR COMPOUNDS*

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Our studies on $K\beta/K\alpha$ X-ray intensity ratios of some of the technologically important $3d$ -transition metal compounds have been reviewed. Comparison of the experimental results with single-configuration Dirac-Fock calculations provided important information on the valence states of the transition metals in various compounds, which can be helpful in understanding the nature of bonding in the compounds.

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1. Introduction

The $K\beta/K\alpha$ X-ray intensity ratio is very sensitive to the change in the valence electronic configuration of $3d$ -transition metals [1]. Here we report the results of our study on some of the technologically important compounds of these metals. The X-ray emission experiments have been carried out using high purity materials, excited by γ -rays of 59.54 keV from a 200 mCi ^{241}Am point-source. The emitted X-rays have been detected by a solid state detector having a resolution (FWHM) of 165 eV at 5.9 keV X-ray energy. The experimental data have been compared with the results of single-configuration Dirac-Fock calculations [1] to get the information about valence electronic structure of the metals in high- T_c YBCO superconductor, $3d$ -metal silicide and boride compounds.

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2. Results and discussion

2.1. YBCO superconductor

The surprising observation in former studies on the change in the T_c of high- T_c superconductors with doping has been a large decrease in T_c by the doping of nonmagnetic dopant Zn in YBCO superconductor. Among others, a change in the Cu($3d$)–O($2p$) hybridization effect has been put forward [2] as one of the reasons for the reduction in T_c . We tried to look into this problem by measuring the $K\beta/K\alpha$ X-ray intensity ratio in Cu, YBCO and Zn doped YBCO. The results are given in Table I. As shown in the table the $K\beta/K\alpha$ intensity ratios of copper in various superconducting compounds are in close agreement with that of pure copper within the experimental error limits, what suggests that the Cu($3d$)–O($2p$) hybridization effect in the superconducting compounds is small and does not change with Zn doping. So the earlier conjecture [2] that a change in the d – p hybridization may be responsible for the decrease in T_c of Zn doped YBCO appears to be not true. A recent report [3] on this problem suggests that scattering of d -wave pairing from Zn impurities is responsible for the decrease in T_c .

TABLE I

Experimental $K\beta/K\alpha$ X-ray intensity ratio of Cu in copper and undoped and Zn doped YBCO superconductors.

Element	Constitution	$K\beta/K\alpha$ X-ray intensity ratio
^{29}Cu	Pure copper	0.1343 ± 0.0014
^{29}Cu	$\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$	0.1371 ± 0.0014
^{29}Cu	$\text{YBa}_2(\text{Cu}_{1-0.033}\text{Zn}_{0.033})_3\text{O}_{7-\delta}$	0.1352 ± 0.0014

2.2. 3d-transition metal silicides

The development of device technology often requires the data from bulk 3d-transition metal silicides to draw firm conclusions about the possible reactions at the metal-semiconductor interfaces. Our results for the disilicide compounds (see Table II) provide an interesting difference between the early disilicide compounds upto Co [4] and late disilicides of Ni and Cu [5]. For Ni and Cu we observe delocalization of 3d electrons whereas for the early disilicides there is an increase of localized 3d electrons possibly due to rearrangement of electrons between 3d and 4s states of the metal or due to transfer of electrons from silicon to the 3d state of the metal.

TABLE II

$K\beta/K\alpha$ X-ray intensity ratios of Ti, V, Cr, Co, Ni, and Cu in pure metals and silicide compounds, the normalized $K\beta$ -to- $K\alpha$ ratios with respect to the pure metals, and the observed change in the number of $3d$ electrons.

Element	Chemical constitution	$K\beta/K\alpha$ intensity ratios	Normalized $K\beta/K\alpha$ ratios	Change in the number of $3d$ electrons
^{22}Ti	Ti	0.1265 ± 0.0006	1.0	—
	TiSi_2	0.1241 ± 0.0005	0.981 ± 0.009	0.7 ± 0.3
^{23}V	V	0.1312 ± 0.0008	1.0	—
	V_3Si	0.1335 ± 0.0008	1.017 ± 0.008	-0.54 ± 0.25
	VSi_2	0.1298 ± 0.0005	0.989 ± 0.010	0.4 ± 0.3
^{24}Cr	Cr	0.1314 ± 0.0008	1.0	—
	Cr_3Si	0.1282 ± 0.0005	0.976 ± 0.008	1.02 ± 0.32
	CrSi_2	0.1259 ± 0.0005	0.958 ± 0.010	1.6 ± 0.3
^{27}Co	Co	0.1335 ± 0.0008	1.0	—
	CoSi_2	0.1310 ± 0.0005	0.981 ± 0.010	1.0 ± 0.4
^{28}Ni	Ni	0.1363 ± 0.0006	1.0	—
	NiSi_2	0.1398 ± 0.0007	1.028 ± 0.007	-1.0 ± 0.4
^{29}Cu	Cu	0.1360 ± 0.0006	1.0	—
	CuSi_2	0.1402 ± 0.0007	1.031 ± 0.007	-1.3 ± 0.4

Our results for V_3Si [6] suggests transfer of about 0.54 ± 0.24 electrons from V to silicon. Alternatively a rearrangement of electrons between $3d$ and $4s$ states of vanadium can also explain the data. Our present finding qualitatively agrees with the theoretical calculation of Bisi and Chiao [7]. The Cr_3Si results suggest that the charge transfer for this compound is opposite to that of V_3Si . This could be the reason why their electronic behaviours are different, V_3Si is a superconductor whereas Cr_3Si is a refractory material with low resistivity.

2.3. $3d$ -transition metal borides

Earlier NMR [8] Hall effect [9] and specific heat [10] studies gave rise to conflicting information in regard to charge transfer from boron to the transition metal atom or vice versa. Our results (see Table III) for CrB and CrB_2 , however, unambiguously suggests that electrons are transferred from boron atom to the $3d$ state of Cr metal. Earlier magnetic [11] and Mössbauer studies [12] on FeB suggested transfer of electrons from boron to iron atom but in our study we did not find any such transfer. Our results

suggest almost no change in the valence electronic structure of Fe in FeB. Our study on TiB₂ also suggested no transfer of electrons (whereas for VB₂ we found transfer of electrons from V to boron) [13].

TABLE III

Same as Table II, but for Ti, V, Cr, and Fe in pure metals and boride compounds.

Element	Chemical constitution	$K\beta/K\alpha$ intensity ratios	Normalized $K\beta/K\alpha$ ratios	Change in the number of 3d electrons
²⁴ Cr	Cr	0.1314±0.0008	1.0	—
	CrB	0.1293±0.0005	0.984±0.008	0.60±0.30
	CrB ₂	0.1288±0.0005	0.980±0.008	0.75±0.30
²⁶ Fe	Fe	0.1307±0.0007	1.0	—
	FeB	0.1311±0.0005	1.003±0.005	-0.17±0.26

3. Conclusions

We find the $K\beta/K\alpha$ X-ray intensity ratio as a powerful study in understanding the valence states of 3d-transition metals in various compounds. Firm conclusions can be drawn from these studies regarding electron transfer and rearrangement between 3d and 4s states of the transition metal. Information from these studies are found to be useful in having a knowledge on the nature of electronic bonding in the 3d-transition metal compounds.

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