

## Influence of solid-state effects on the $K\beta$ -to- $K\alpha$ x-ray intensity ratios of Ni and Cu in various silicide compounds

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(Received 13 December 1996; revised manuscript received 2 February 1998)

$K\beta$ -to- $K\alpha$  x-ray intensity ratios of Ni and Cu in various silicide compounds  $\text{Ni}_2\text{Si}$ ,  $\text{NiSi}$ ,  $\text{Ni}_2\text{Si}_3$ ,  $\text{NiSi}_2$ ,  $\text{Cu}_2\text{Si}$ ,  $\text{CuSi}$ , and  $\text{CuSi}_2$  have been measured following excitation by 59.54 keV  $\gamma$  rays from a 200 mCi  $^{241}\text{Am}$  point source. Comparison of the intensity ratios for Ni with the multiconfiguration Dirac-Fock calculations indicates decreasing  $3d$  electron population with the increase of silicon concentration, a trend similar to the one predicted by the previous theoretical calculations [O. Bisi and C. Calandra, *J. Phys. C* **14**, 5479 (1982)]. However, quantitatively our results for the Ni  $3d$  electron population are different from the results reported there. The intensity ratios for Ni and Cu in disilicide compounds indicate enhancement of the  $K\beta$ -to- $K\alpha$  ratio over the pure metal values, but for the other silicide compounds the Ni intensity ratios show opposite behavior than Cu, suggesting a difference in the nature of electron delocalization.

[S0163-1829(98)04737-7]

### I. INTRODUCTION

The structural and electronic properties of  $3d$  metal silicides are receiving increasing attention in connection with efforts to understand the behavior of the reactive Si-metal interfaces.<sup>1</sup> Most  $3d$  transition metals and near noble metals can react with silicon to form thin silicidelike phases. These phases play a very important role in determining the properties of electronic devices and the study of their electronic structure is of paramount importance.

To better understand chemical bonding at the interface and to identify potential structural and electronic differences between bulk silicide and these silicidelike phases, one must examine both bulk and interface silicides. However, very little is known about the electronic structure of bulk silicides. In this paper we present our experimental results on relative  $K$  x-ray intensities of Ni and Cu in various silicide compounds. In the past, the study of relative  $K$  x-ray intensities had provided useful information on the electronic structure of  $3d$  transition metals in their alloys and compounds.<sup>2-14</sup> Previous study on the electronic structure of bulk Ni silicides from photoelectron energy distribution measurements by Franciosi, Weaver, and Schmidt<sup>15</sup> revealed interesting differences in electronic bonding in  $\text{Ni}_2\text{Si}$ ,  $\text{NiSi}$ , and  $\text{NiSi}_2$ . Their study had also suggested that the Ni  $d$  character becomes more atomiclike as the Ni concentration decreases. Theoretical calculations<sup>16</sup> also confirmed this trend, showing the electronic configuration of Ni to go from about  $3d^{8.7}4sp^{1.2}$  in  $\text{Ni}_2\text{Si}$  to  $3d^{8.6}4sp^{1.3}$  in  $\text{NiSi}$  and  $3d^{8.3}4sp^{1.5}$  in  $\text{NiSi}_2$ .

In a number of x-ray spectral studies of  $3d$  transition metals, it has been observed that the  $K\beta$ -to- $K\alpha$  intensity ratios are dependent on the physical and chemical environments of the elements in the samples. In studies of  $3d$  metal compounds,<sup>4-14</sup> the influence of chemical effects has shown differences in the  $K\beta$ -to- $K\alpha$  ratios up to nearly 10%. Such

chemical effects can be caused either by contraction of  $3p$  orbitals, which is in turn due to a screening altered by a varying  $3d$  charge delocalization, or by the admixture  $p$  states from the ligand atoms to the  $3d$  state of the metal through  $d$ - $p$  hybridization, or both. In  $3d$  metal compounds, the  $d$ - $p$  hybridization along with  $3d$  electron delocalization are responsible for the observed change in the  $K\beta$ -to- $K\alpha$  intensity ratio, whereas in alloys<sup>2,3,10</sup> the  $3d$  electron transfer/delocalization is responsible for the observed change in the  $K\beta$ -to- $K\alpha$  ratio.

The aim of the present study has been to measure the  $K\beta$ -to- $K\alpha$  x-ray intensity ratios for Ni and Cu in various silicide compounds and provide an explanation of these ratios based on reliable theoretical calculations. In a 1989 paper, Jankowski and Polasik<sup>17</sup> proposed a special average-level (SAL) version of multiconfiguration Dirac-Fock (MCDF) calculation that gives values of the  $K\beta$ -to- $K\alpha$  intensity ratios for Ti, Cr, Fe, Ni, Cu, Zn, and Ge in a significantly better agreement with high-accurate experimental data of Perujo *et al.*<sup>18</sup> than the theoretical predictions of Scofield<sup>19</sup> and the results of standard average-level (AL) and extended average-level (EAL) versions of MCDF calculations (see Grant *et al.*<sup>20</sup>). Therefore, in order to provide a proper interpretation of the observed  $K\beta$ -to- $K\alpha$  x-ray intensity ratios for Ni and Cu in various silicide compounds, and to obtain information about the valence electronic structure of the metals in these compounds, the MCDF calculations in the SAL version have been carried out on Ni and Cu for various electronic configurations of the type  $3d^{m-r-t}4s^r4p^t$  ( $r, t = 2, 1, 0$  and  $m$  stands for the total number of valence electrons in the atom). The theoretical calculations presented in this paper have been done using the atomic MCDF package developed by Grant *et al.*<sup>20,21</sup>

### II. EXPERIMENTAL DETAILS

The experiments were carried out using thick samples procured from the Goodfellow company, UK. The Ni and Cu

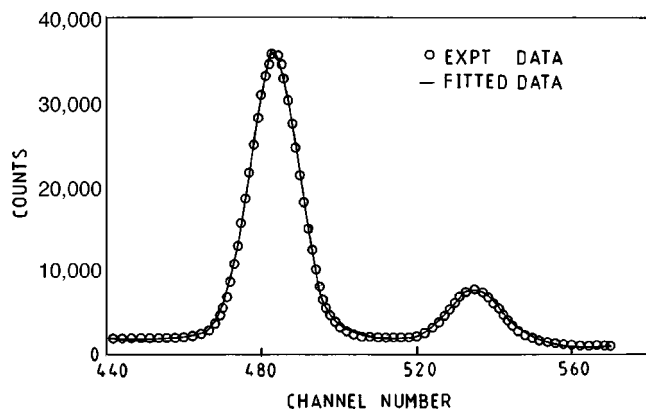


FIG. 1. A typical K x-ray spectrum of Ni in NiSi<sub>2</sub>.

silicide compounds for which measurements have been made are NiSi<sub>2</sub>, Ni<sub>2</sub>Si<sub>3</sub>, NiSi, Ni<sub>2</sub>Si, CuSi<sub>2</sub>, CuSi, Cu<sub>2</sub>Si. Gamma rays of 59.54 keV from a 200 mCi <sup>241</sup>Am point source were used to ionize the target atoms and the emitted x rays were detected by a 30 mm<sup>2</sup>×3 mm-thick Canberra Si(Li) detector having a 12.7 μm-thick beryllium window. The resolution of the Si(Li) detector was ~165 eV (full width at half maximum) for a 5.9 keV x-ray peak. Details of the experimental arrangements can be found in our earlier paper.<sup>2</sup>

Pulses from the Si(Li) detector preamplifier were fed to an ORTEC-572 spectroscopy amplifier and then recorded in a Canberra PC based Model S-100 multichannel analyzer. The gain of the system was maintained at ~30 eV/channel. The counting was continued until the counts under the less intense Kβ peak were around 5×10<sup>4</sup>. A typical K x-ray spectrum of Ni in NiSi<sub>2</sub> is shown in Fig. 1.

### III. DATA ANALYSIS

All the x-ray spectra were carefully analyzed with a multi-Gaussian least-squares fitting program<sup>23</sup> using a non-linear background subtraction. No low-energy tail was included in the fitting as its contribution to the ratio was shown to be quite small.<sup>24</sup> A residue spectrum corresponding to the x-ray spectrum of Fig. 1 is shown in Fig. 2. This figure suggests that the fit is quite satisfactory. The Kβ-to-Kα in-

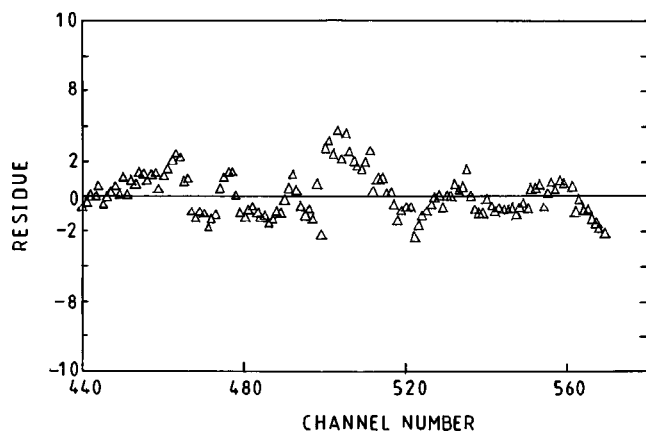


FIG. 2. Residues corresponding to the K x-ray spectrum of Fig. 1.

tensity ratios were determined from the fitted peak areas after applying necessary corrections to the data.

### IV. CORRECTIONS

Corrections to the measured ratios mainly come from the difference in the Kα and Kβ self-attenuations in the sample, difference in the efficiency of the Si(Li) detector, and air absorption on the path between the sample and the Si(Li) detector window. The efficiency of the detector is estimated theoretically, as mentioned in our previous paper.<sup>3</sup> Our theoretically estimated efficiency was shown to be in good agreement with the measured efficiency.<sup>25</sup> It has been found that the discrepancy between the measured and theoretical efficiency at the energy region of present interest was ≤1.0%. The correction due to the Si(Li) detector relative efficiency to the measured Kβ-to-Kα ratio is found to be ≤1%.

The major correction to the measured Kβ-to-Kα ratio stems from the self-absorption in the target. Since our results for pure metals agree very well with the earlier thin target results of Slivinsky and Ebert<sup>24</sup> and Paic and Pecar,<sup>26</sup> we are confident that our correction for the self-absorption is quite satisfactory. This correction was estimated using the method as described in our earlier paper.<sup>3</sup> The correction for the air path was also estimated in a manner similar to the one described before.<sup>3</sup> For the estimation of these corrections the mass attenuation coefficients were taken from the computer program XCOM by Berger and Hubbell.<sup>22</sup> The absorption corrections for the various compounds are estimated using the values of Ni, Cu, and Si in the following Bragg's-rule formula:

$$(\mu/\rho) = \sum_i w_i \mu_i / \rho_i, \quad (1)$$

where,  $w_i$  is the proportion by weight of the  $i$ th constituent and  $\mu_i/\rho_i$  is the mass attenuation coefficient for the  $i$ th constituent in the compound.

The statistical error contributing to the measured Kβ-to-Kα ratio is calculated by the least-squares fitting program.<sup>23</sup> The total uncertainty in the relative Kβ-to-Kα ratios with respect to the pure metal is expected to be quite small (≤1%).

### V. THEORETICAL CALCULATIONS

The MCDF method applied in the present study has been mainly developed by Grant *et al.* and is described in detail in several papers.<sup>20,21,27-31</sup> Moreover, all the basic ideas of the alternative SAL version of the MCDF calculations, which are used in this work, have been presented by Jankowski and Polasik.<sup>17</sup> However, for the sake of clarity, some essential details are very briefly recapitulated below.

The Hamiltonian for the  $N$ -electron atom is taken in the form

$$H = \sum_{i=1}^N h_D(i) + \sum_{j>i=1}^N C_{ij}, \quad (2)$$

where  $h_D(i)$  is the Dirac operator for  $i$ th electron and the terms  $C_{ij}$  account for electron-electron interactions and come from one-photon exchange process. The latter are a sum of the Coulomb interaction operator and the transverse Breit

TABLE I. Relative  $K\beta$ -to- $K\alpha$  intensity ratios of Cu and Ni in different silicide compounds. The errors quoted are statistical only.

Element	Constitution	$K\beta$ -to- $K\alpha$ Intensity ratios	Relative $K\beta$ -to- $K\alpha$ Intensity ratios Normalized to pure element results
$^{28}\text{Ni}$	Ni	$0.1363 \pm 0.0006$	1.0
	$\text{Ni}_2\text{Si}$	$0.1315 \pm 0.0007$	$0.965 \pm 0.007$
	NiSi	$0.1300 \pm 0.0007$	$0.954 \pm 0.007$
	$\text{Ni}_2\text{Si}_3$	$0.1324 \pm 0.0007$	$0.971 \pm 0.007$
	NiSi <sub>2</sub>	$0.1398 \pm 0.0007$	$1.028 \pm 0.007$
$^{29}\text{Cu}$	Cu	$0.1360 \pm 0.0006$	1.0
	$\text{Cu}_2\text{Si}$	$0.1371 \pm 0.0007$	$1.008 \pm 0.007$
	CuSi	$0.1378 \pm 0.0007$	$1.013 \pm 0.007$
	$\text{CuSi}_2$	$0.1402 \pm 0.0007$	$1.031 \pm 0.007$

operator. The atomic state functions with the total angular momentum  $J$  and parity  $p$  are represented in the multiconfigurational form

$$\Psi_s(J^p) = \sum_m c_m(s) \Phi(\gamma_m J^p), \quad (3)$$

where  $\Phi(\gamma_m J^p)$  are configuration state functions (CSF's),  $c_m(s)$  are the configuration mixing coefficients for state  $s$ ,  $\gamma_m$  represents all information required to uniquely define a certain CSF.

In the SAL version of the MCDF calculations, the energy functional is specially averaged over all the initial and final states and can be expressed by

$$E = E_{opt} + \sum_a \bar{q}_a \epsilon_a S(a, a) + \sum_{\substack{a,b \\ a \neq b}} \epsilon_{a,b} S(a, b), \quad (4)$$

where  $\bar{q}_a$  is the generalized occupation number for the orbital  $a$ ,  $\epsilon_a$  and  $\epsilon_{ab}$  are the Lagrange multipliers,  $S(a, b)$  is the overlap integral, and  $E_{opt}$  is taken in the form

$$E_{opt} = \frac{1}{3} \left[ \frac{1}{n_i} \sum_{i=1}^{n_i} H_{ii} + \frac{1}{n_j} \sum_{j=1}^{n_j} H_{jj} + \frac{1}{n_k} \sum_{k=1}^{n_k} H_{kk} \right], \quad (5)$$

where  $H_{ii}$ ,  $H_{jj}$ , and  $H_{kk}$  are the diagonal contributions to the Hamiltonian matrix,  $n_i$  is the number of all the CSF's defining the initial states (of the type  $1s^{-1}$ ), and  $n_j$  and  $n_k$  are the numbers of all the CSF's defining the final states of the types  $2p^{-1}$  and  $3p^{-1}$ , respectively.

In this version of the calculation, the common set of the orbitals for all the initial and final states is to be determined. This removes the problem of nonorthogonality of the orbitals and, moreover, greatly reduces the computational effort, as only the coefficients  $c_m(s)$  have to be determined for each state by diagonalizing the matrix of the Hamiltonian in the space of relevant CSF's.

Apart from the transverse (Breit) interaction, two types of quantum electrodynamics (QED) corrections are included, namely the self-energy and vacuum polarization corrections (see McKenzie, Grant, and Norrington<sup>21</sup>). The formulas for the transition matrix elements and spontaneous emission probabilities can be found in the work of Grant.<sup>27</sup> The calculations have been performed for both the Coulomb and

Babushkin<sup>32,33</sup> gauges. In the nonrelativistic limit the Coulomb gauge formula for the electric dipole transitions yields the dipole velocity expression while the Babushkin formula gives the dipole length expression.<sup>27</sup>

## VI. RESULTS AND DISCUSSION

The experimental results for the  $K\beta$ -to- $K\alpha$  x-ray intensity ratios of Ni and Cu for the case of pure metals and in various silicide compounds are presented in Table I. The results for both Ni and Cu in the disilicides show a similar kind of enhancement over the pure metal values. However, for the other compounds the results for Ni show an opposite behavior as compared to Cu, i.e., the results for Ni are lower than the pure metal value, whereas for Cu they are somewhat higher than the pure metal value.

As has been mentioned in the Introduction, the SAL version of the MCDF method gives values of the  $K\beta$ -to- $K\alpha$  intensity ratios for  $3d$  transition-metal atoms in a significantly better agreement (see Jankowski and Polasik<sup>17</sup>) with high-accurate experimental data of Perujo *et al.*<sup>18</sup> than the theoretical predictions of Scofield<sup>19</sup> and the results of standard AL and EAL versions of the MCDF calculations. Therefore, detailed MCDF calculations in the SAL version with the inclusion of the transverse (Breit) interaction and QED (self-energy and vacuum polarization) corrections have been carried out for Ni and Cu atoms to explain reliably the dependence of  $K\beta$ -to- $K\alpha$  x-ray intensity ratios on changes in configurations of the valence electrons that provide interpretation of the observed  $K\beta$ -to- $K\alpha$  x-ray intensity ratios for Ni and Cu in various silicide compounds. We have not considered any  $d$ - $p$  hybridization effect between  $3d$  electrons of the metal and  $3p$  electrons of silicon in the calculation, although there is a signature of this effect as had been shown earlier by photoelectron energy distribution spectral studies.<sup>15</sup>

The results of the MCDF calculations are presented in Table II. In each case the Coulomb and Babushkin gauge formulas for the electric dipole transitions have been used. It can be found from Table II that for both Ni and Cu atoms, the greatest values of the  $K\beta$ -to- $K\alpha$  intensity ratios are for a  $3d^{m-4}4s^24p^2$  configuration type, but the smallest values are for configurations  $3d^{10}$  in the case of Ni and  $3d^{10}4s^1$  in the case of Cu.

TABLE II. The theoretical MCDF  $K\beta$ -to- $K\alpha$  intensity ratios of Ni and Cu corresponding to various types of the electronic configurations. In each case the Coulomb and Babushkin gauges have been used.

Element	Z	Electronic configuration	The $K\beta$ -to- $K\alpha$ intensity ratios	
			Coulomb gauge	Babushkin gauge
Ni	28	$3d^6 4s^2 4p^2$	0.1439	0.1452
		$3d^7 4s^2 4p^1$	0.1397	0.1410
		$3d^8 4s^2$	0.1361	0.1374
		$3d^9 4s^1$	0.1333	0.1346
		$3d^{10}$	0.1313	0.1325
Cu	29	$3d^7 4s^2 4p^2$	0.1438	0.1450
		$3d^8 4s^2 4p^1$	0.1399	0.1410
		$3d^9 4s^2$	0.1366	0.1377
		$3d^{10} 4s^1$	0.1340	0.1350

The experimental results for the  $K\beta$ -to- $K\alpha$  ratios of Ni in different silicide compounds have been compared with the MCDF results in Fig. 3. The calculation based on the Babushkin gauge give higher  $3d$  electron population than those obtained by comparing the experimental data with the calculation of Coulomb gauge. As is seen from Fig. 3, the  $3d$  electron population increases with the decrease of Ni concentration, a trend similar to the theoretical results reported earlier.<sup>16</sup> But quantitatively our results for the Ni  $3d$  electron population are different from the results reported in that work. Our  $3d$  electron populations for  $Ni_2Si_3$ , NiSi, and  $Ni_2Si$  are higher than the atomic value, whereas for  $NiSi_2$  it is less than the atomic value (electronic configuration  $3d^8 4s^2$ ). The  $d$ - $p$  hybridization effect that increases the  $K\beta$ -to- $K\alpha$  ratio should not be the cause for the observed decrease in the  $K\beta$ -to- $K\alpha$  ratio in  $Ni_2Si_3$ , NiSi, and  $Ni_2Si$ .

The Cu results are compared with the MCDF predictions in Fig. 4. The predicted electronic configurations for the three compounds show a lower  $3d$  electron population than that of solid Cu. The  $K\beta$ -to- $K\alpha$  ratios of Cu for  $CuSi_2$  is

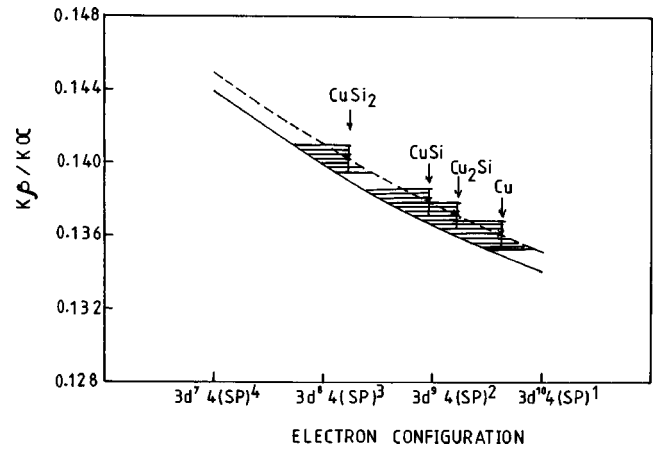


FIG. 4. Comparison of the experimental  $K\beta$ -to- $K\alpha$  intensity ratio of Cu in different Cu silicides with the predictions of MCDF calculations; the solid line corresponds to theoretical results based on the Coulomb gauge and the dashed line corresponds to Babushkin gauge. The shaded regions correspond to the ranges of electronic configurations for which the experimental values overlap with the results of the theoretical calculations.

enhanced as in the case of  $NiSi_2$ . But the results for the other compounds of Cu show an opposite behavior to the Ni results, copper showing a somewhat enhanced  $K\beta$ -to- $K\alpha$  ratio, whereas the nickel results show a decrease in the ratio, meaning thereby that for these compounds the nature of  $3d$  electron delocalization is opposite for the two metals.

## VII. CONCLUSIONS

On the basis of experimental results of the  $K\beta$ -to- $K\alpha$  x-ray intensity ratios of Ni and Cu in various silicide compounds as well as detailed separate MCDF calculations on Ni and Cu for various electronic configurations, some general conclusions can be drawn.

In disilicide compounds, both Ni and Cu indicate similar enhancement of the  $K\beta$ -to- $K\alpha$  intensity ratio over the pure metal values. For the other compounds the results for Ni

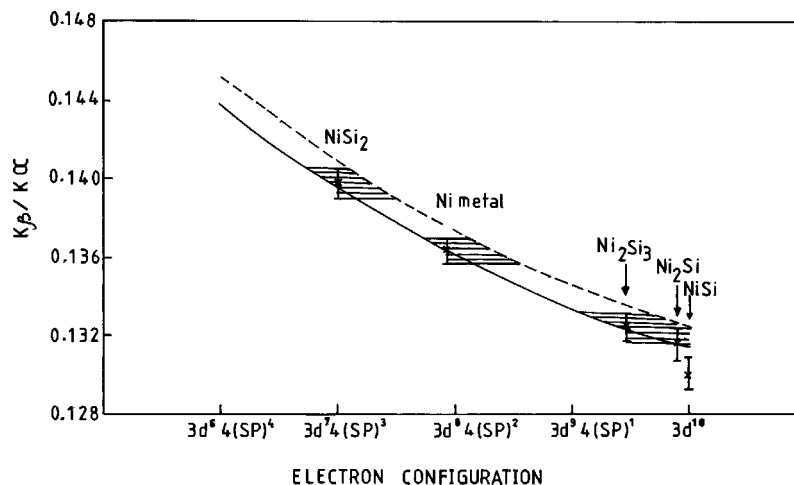


FIG. 3. Comparison of the experimental  $K\beta$ -to- $K\alpha$  intensity ratio of Ni in different Ni silicides with the predictions of MCDF calculations; the solid line corresponds to theoretical results based on the Coulomb gauge and the dashed line corresponds to Babushkin gauge. The shaded regions correspond to the ranges of electronic configurations for which the experimental values overlap with the results of the theoretical calculations.

show an opposite behavior than for Cu. Our present results do not agree quantitatively with the previous theoretical calculations on the valence electron configurations of Ni silicides,<sup>16</sup> although the trend seems to be similar.

The authors believe that the results of this study will be helpful in better understanding the dependence of  $K\beta$ -to- $K\alpha$  x-ray intensity ratios on changes in configurations of the valence electrons and throw some new light on the valence electronic structure of Ni and Cu in their silicide compounds. Moreover, the results of this work can stimulate both the

experimental and theoretical research with other silicide compounds that have lots of technological applications.

#### ACKNOWLEDGMENTS

This work was supported in part by the Council of Scientific and Industrial Research, India and partly by the Polish Committee for Scientific Research (KBN), Grant No. 2 P03B 055 09.

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