# Splitting of the 3*p* levels in the transition elements and their oxides

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Systematic measurements have been made on the  $K\beta_{1,3}$  emission lines of the transition elements  $21 \le Z \le 29$ . Each element was studied in the metallic state and also in one of its oxidized states. The energy separation  $\Delta E$  between the  $3p_{1/2}$  and the  $3p_{3/2}$  levels in these elements varies from about 3.4 eV for  $^{29}$ Cu to about 2.0 eV for  $^{21}$ Sc, and therefore the  $K\beta_{1,3}$  complex almost appears as a single emission line under the present experimental conditions. The exchange interaction between the 3d and the 3p electrons in these elements causes some of the electrons in the 3p state to move to lower energy levels; transitions from these levels appear as emission bands at the low-energy side of the  $K\beta_{1,3}$  complex. A computer program was devised to unfold the complex structures and provide values for the mean energy separation  $\Delta E$  and the relative transition probabilities of the constituent lines. For all the elements studied, the effect of oxidation seems to enhance the relative intensity of the low-energy emission band, without significantly altering the value of  $\Delta E$ . Comparison of the present experimental results with theoretical values derived on the basis of a simple exchange interaction exhibits good agreement on the value of the mean energy separation  $\Delta E$ , but shows large discrepancies in the relative transition probabilities.

#### INTRODUCTION

The transition elements have partially filled 3d shells, resulting in an electronic configuration parallel to that existing in the rare-earth elements where the interaction between the 4f and the 4d electrons splits both levels and results in sets of x-ray emission lines that are characteristic of the rare-earth elements alone, <sup>1-3</sup> and where energy shifts of x-ray lines from different chemical compounds has been observed and has been qualitatively explained on the basis of free-ion relativistic self-consistent-field calculations.<sup>4,5</sup>

The interaction between the 3d electrons and the  $2p_{1/2}$  and the  $2p_{3/2}$  levels splits both levels,<sup>6</sup> and produces the asymmetry observed in the  $K\alpha_1$  and  $K\alpha_2$  x-ray lines of the transition elements,<sup>7,8</sup> and the abnormally large physical width of these lines.<sup>8</sup> It also manifests itself in the irregular shape of the  $K\beta/K\alpha$  radiative transition rate in this region of the atomic spectra.<sup>9,10</sup> Although some work has been done on the effect of unpaired valence electrons on the photoabsorption spectra of both rareearth and transition elements, very little study has been performed on the emission band that accompanies the  $K\beta_{1,3}$  complex in the transition elements.<sup>11</sup> The photoemission work in Ref. 11 is a study of the splitting of the 2p and 3p levels of manganese in a single crystal of MnF<sub>2</sub>.

In this work systematic study has been made on the  $K\beta_{1,3}$  emission lines of the following elements: <sup>30</sup>Zn, <sup>29</sup>Cu, <sup>28</sup>Ni, <sup>27</sup>Co, <sup>26</sup>Fe, <sup>25</sup>Mn, <sup>24</sup>Cr, <sup>23</sup>V, <sup>22</sup>Ti, and <sup>21</sup>Sc, both in the metallic state, and in the following oxidized states: CuO, NiO, Co<sub>3</sub>O<sub>4</sub>, Fe<sub>2</sub>O<sub>3</sub>,  $MnO_2$ ,  $Cr_2O_3$ , VO, and  $TiO_2$ . The higher-Z elements, namely <sup>31</sup>Ga and <sup>32</sup>Ge, were also investigated to observe if this effect persists after the 3d shell is completely full. Calculations were made by Tsutsumi, <sup>12</sup> by Nefedov, <sup>13</sup> and by Ekstig *et al.*, <sup>14</sup> to explain the type of electronic interaction that produces such a level splitting. Theoretical values are later compared with the present experimental results.

#### **EXPERIMENTAL**

Thick polished metallic blocks with better than 99.9% purity were used as targets for all the elements studied except <sup>21</sup>Sc, where a thin foil of the elements (0.13 mm thick) was used. The <sup>21</sup>Sc foil was held against a Cu block by a set-screw during bombardment.

The oxide samples studied were 99.9% pure and were transformed into glassy pellets in a KBr pellet press. A pellet is placed at the surface of a copper dish filled with melted <sup>31</sup>Ga. The pellet is then gently pressed into the gallium until the surface of the pellet and that of the copper dish were in the same plane. The gallium solidifies, holding the pellet in this position and insuring good thermal contact. The pellets were large enough so that only a portion of their surface was exposed to the bombarding electron beam; thus when the heat melted portions of the gallium the pellet position was not altered. This arrangement has been previously tested and proven satisfactory in the study of the rare-earth elements and their oxides.2,15

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All samples studied were tightly fitted to a water-cooled anode assembly and then introduced into a locally designed and constructed x-ray tube which is continuously pumped to a pressure of about  $10^{-6}$  mm of Hg.

A tungsten filament fitted in a stainless-steel focusing cup provides an electron beam of constant energy and flux to excite the target elements. An insulating transformer supplied the tungsten filament with the necessary heating current. A power supply connected in series with a voltage regulator and ripple suppressor and capable of delivering a steady voltage with less than 0.3% ripple at a full load of 120 keV and 30 mA was used to accelerate the electron beam. Generally, the power on the tube, during this experiment, was limited to about 0.6 mA and 35 keV.

The emission spectra of the studied samples were analyzed by means of a modified singlecrystal high-angle goniometer and a NaI scintillation detector. The intensity of the emission lines and the accompanying profiles was measured by stepping the goniometer through the Bragg angle  $2\theta$  in steps of 0.005 degree. At each position the number of counts was recorded for three one-minute intervals and averaged. Because of the low intensity from the low-Z oxide samples (VO and TiO<sub>2</sub>), longer counting periods were used. Several runs were made for each of the studied samples, but only the average values are reported.

Figure 1 is the  $K\beta_{1,3}$  emission spectrum of Mn from metallic Mn (solid curve), and from MnO<sub>2</sub>



FIG. 1.  $K\beta_{1,3}$  emission spectrum of manganese from metallic Mn (solid curve) and from MnO<sub>2</sub> (dashed curve). The two spectra were computer-normalized to the same peak intensity and then superimposed.

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### DATA ANALYSIS

The observed photon frequency distribution  $f(\nu)$  within an x-ray emission line may be written as:

$$f(\nu) = \int_{-\infty}^{\infty} \Psi(\nu') \phi(\nu - \nu') d\nu', \qquad (1)$$

where  $\Psi$  is the physical photon distribution and  $\phi$  is the instrumental response. Generally good fits may be obtained by assuming a Lorentzian x-ray line shape and a Gaussian instrumental response.<sup>16,17</sup> However, for deducing peak separation and relative intensities, instead of looking at  $\psi(\nu)$ , one can treat  $f(\nu)$  directly. The experimental data from a given run is computer-fitted to a function of the form

$$f(\nu_{i}) = P(1) + P(2)\nu_{i} + P(3) \exp\left(G \frac{P(4) - \nu_{i}}{P(5)}\right) + \frac{P(3)}{2} \exp\left(G \frac{P(4) - \nu_{i} - \delta}{P(5)}\right) + P(6) \exp\left(G \frac{P(7) - \nu_{i}}{P(8)}\right), \quad (2)$$



FIG. 2. Computer fit to the  $K\beta_{1,3}$  emission lines of iron from an Fe<sub>2</sub>O<sub>3</sub> sample, separating the experimental data into a  $K\beta_{1,3}$  line and a single nondiagram line. The indicated widths are total widths. The instrumental width at this energy is 3.9 eV (see Ref. 8).

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where  $\nu_i$  is the frequency at each data point,  $G = -4 \ln 2$ ,  $\delta$  is the frequency separation between  $K\beta_1$  and  $K\beta_3$ , and where the fitted parameters P(1) through P(8) stand for the following quantities: P(1), the background; P(2), the slope of background; P(3), the  $K\beta_1$  peak height; P(4), the  $K\beta_1$ peak position; P(5), the  $K\beta_1$  linewidth; P(6), the peak height of nondiagram line; P(7), the peak position of nondiagram line; and P(8), the width of nondiagram line. Here it is assumed that the intensity of the  $K\beta_3$  line is half that of the  $K\beta_1$ line and that the  $K\beta_1$  and  $K\beta_3$  lines have the same physical width. Thus in Eq. (2), the third term represents the  $K\beta_1$  line, the fourth term represents the  $K\beta_3$  line, and the last term represents the nondiagram line. A computer fit separating the experimental data into a  $K\beta_{1,3}$  line and a single nondiagram line is shown in Fig. 2. The width of the nondiagram lines and the presence of structure on their profiles, especially at low Z, leads one to believe that several transitions are involved.

## **RESULTS AND DISCUSSION**

The measured values of the mean energy separation  $\Delta E$  between the diagram and nondiagram emission lines as well as their relative transition probabilities A'/A are summarized in Table I, and are plotted as a function of atomic numbers in Fig. 3. Here A' is the integrated area under the nondiagram emission peak, while A is the integrated area under the  $K\beta_{1,3}$  emission peak. For comparison, theoretical values from Ref. 12 are included in Table I and in Fig. 3 as well.

The energy separation caused by the exchange interaction between the 3p hole and the partially filled 3d level is given by<sup>12</sup>

$$\Delta E = (2S+1) \left[ \frac{2}{15} G^1(3p3d) + \frac{3}{15} G^3(3p3d) \right], \qquad (3)$$

where S is the total spin of the 3d electrons (see Table I) and  $G^1$  and  $G^3$  are the Hartree-Fock-Slater integrals whose values were computed by Mann.<sup>18</sup> This simple theory gives the relative transition probability as being equal to the level multiplicity

$$A'/A = S/(S+1)$$
. (4)

Values of  $\Delta E$  and A'/A were thus calculated and included in Table I and Fig. 3 for comparison. The errors quoted in Table I and shown as error bars in Fig. 4, are statistical errors obtained from the error matrix of the least-squares-fit program. They vary in value from a low of about 10% for the elements <sup>22</sup>Ti to <sup>27</sup>Co where both  $\Delta E$  and A'/A are relatively large, to a high of about 20% for <sup>29</sup>Cu, where the value of A'/A drops to about 6% only.

Figure 3 shows that for the mean energy separation  $\Delta E$  between the diagram lines  $(K\beta_{1,3})$ and the nondiagram lines, the agreement between theory and experiment is good, and except for a few points all calculated values fall within experimental errors from the measured ones. Thus one may conclude that Eq. (3) provides a reasonably good gross description of the energy separation caused by the partially filled 3d level; on the other hand, the values of the relative transition probabilities A'/A given by Eq. (4) are two to four times as large as the measured values. Thus it becomes obvious that radiative emission from these split levels involves more than the multiplicity of these levels.

It should be noted that the oxide samples gave, in general, larger values of A'/A than the metal samples, while the energy separations were basically the same for both metals and oxides. A change in the 3d4s electron configuration of



FIG. 3. Relative transition probabilities of the nondiagram lines to the  $K\beta_{1,3}$  lines (A'/A), plotted as a function of atomic numbers (top), and the energy separation E (eV) between the  $K\beta_{1,3}$  and the nondiagram lines, plotted as a function of atomic numbers (bottom).

TABLE I. The 3d4s electron configuration of the transition elements, their ground term, and the spin of the 3d electrons; the mean energy separation  $\Delta E$  and the relative transition probabilities A'/A. The quoted errors are statistical and were obtained from the error matrix of the least-squares-fit program. (0.00 indicates measured and found to be zero.)

	Electron	Ground	Spin of the 3d electrons	$\Delta E$ (eV) Experiment			A'/A Experiment		
Element	configuration	term	S	Theory	Metal	Oxides	Theory	Metal	Oxides
<sup>20</sup> Ca	$3d^{0}4s^{2}$	<sup>1</sup> S <sub>0</sub>	0	0.00	••••		0	•••	a
$^{21}$ Se	$3d^{1}4S^{2}$	${}^{2}D_{3/2}$	$\frac{1}{2}$	3.71	$5.73 \pm 0.86$	•••	<u>1</u> 3	$0.069 \pm 0.01$	•••
$^{22}\mathrm{Ti}$	$3d^{2}4S^{2}$	${}^{3}F_{2}$	1	6.22	$7.08 \pm 0.71$	$5.80 \pm 0.70$	$\frac{1}{2}$	$0.102 \pm 0.01$	$0.183 \pm 0.027$
<sup>23</sup> V	$3d^{3}4S^{2}$	${}^{4}F_{3/2}$	$\frac{3}{2}$	9.07	$10.24 \pm 1.09$	$9.51 \pm 1.0$	3	$0.163 \pm 0.016$	$0.250 \pm 0.025$
$^{24}Cr$	$3d^{5}4S^{1}$	${}^{7}S_{3}$	<u>5</u> 2	13.35	$11.04 \pm 1.11$	$10.62 \pm 1.1$	57	$0.234 \pm 0.023$	$0.292 \pm 0.029$
<sup>25</sup> Mn	$3d^{5}4S^{2}$	<sup>6</sup> S <sub>5/2</sub>	52	15.65	$12.28 \pm 1.2$	$12.87 \pm 1.3$	57	$\textbf{0.302} \pm \textbf{0.030}$	$0.326 \pm 0.033$
$^{26}$ Fe	$3d^{6}4S^{2}$	${}^{5}D_{4}$	2	13.84	$11.71 \pm 1.2$	$13.36 \pm 1.3$	<u>2</u> 3	$0.344 \pm 0.034$	$\textbf{0.394} \pm \textbf{0.039}$
<sup>27</sup> Co	$3d^{7}4S^{2}$	${}^{4}F_{9/2}$	<u>3</u> 2	11.69	$11.54 \pm 1.1$	$12.19 \pm 1.2$	35	$0.157 \pm 0.016$	$0.255 \pm 0.026$
<sup>28</sup> Ni	$3d^{8}4S^{2}$	${}^{3}\!F_{4}$	1	9.22	$12.98 \pm 1.9$	$11.29 \pm 1.7$	$\frac{1}{2}$	$\boldsymbol{0.112 \pm 0.020}$	$0.062 \pm 0.02$
<sup>29</sup> Cu	$3d^{10}4S^{1}$	${}^{2}S_{1/2}$	0	0.00	$12.34 \pm 2.4$	$12.81 \pm 2.5$	0	$\textbf{0.062} \pm \textbf{0.020}$	$0.063 \pm 0.02$
<sup>30</sup> Zn	$3d^{10}4S^2$	<sup>1</sup> S <sub>0</sub>	0	0.00	0.00	0.00	0	0.00	0.00

<sup>a</sup> Not measured.

one of these atoms (i.e., placing the atom in different chemical compounds), results in a considerable change in the energy of its inner electronic levels, but all the levels are shifted in the same direction so that the net change in the energy difference between two levels is small, giving rise to a small energy shifts of the emission lines.<sup>4,5</sup> The investigation of such a small shift requires more careful measurements. All the calculations that deal with the types of electronic interactions that produce such level splittings<sup>12-14</sup> were made for a free atom in space, while the experiments are performed on atoms either in a metal block or in an oxide; in either case the 3d4s electronic configuration is not the same as

that of a free atom. In an isolated atom the energy of the 4s state lies below that of the 3dstate, but as the atoms are brought together to form metals or oxides, the wave functions of the states overlap, resulting in a broadening of the unique energy levels into energy bands. The overextended 4s wave function now overlaps in neighboring atoms, and some of the states in the 4s band possess energies higher than those of the 3d band.<sup>19</sup>

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