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X-RAY PHOTOELECTRON SPECTROSCOPY OF SOME NICKEL AND IRON COMPOUNDS

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Leslie Oga Pont  
(M.S. thesis)

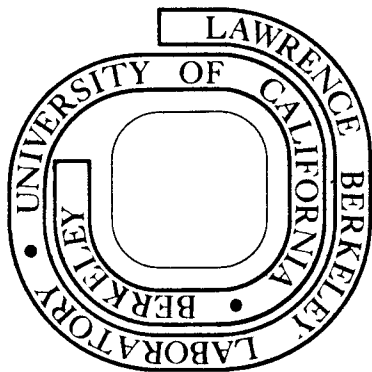
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X-RAY PHOTOELECTRON SPECTROSCOPY OF SOME  
NICKEL AND IRON COMPOUNDS

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Abstracts

I. Nickel

The X-ray photoelectron spectra of 14 nickel compounds were investigated to determine the nickel 3p and  $2p_{3/2}$  binding energies. Referencing problems encountered with carbon were eliminated by internal referencing against vacuum deposited gold. Peak resolution was complicated by shake-up transitions and multiplet splitting. The data show a general trend of increasing binding energy with increasing nickel oxidation state, but an absolute correlation is not possible without considering the number and electronegativity of ligands and their binding to nickel.

II. Iron

X-ray photoelectron spectra were taken of six iron compounds. Some of these compounds have been investigated previously, but the iron 3p binding energies did not correlate well with oxidation state. Our data were referenced against gold and our binding energies were aligned with those in an earlier work. The iron binding energies appear to depend on the iron atomic charge and on the electronegativity and number of ligands.

Paper I. Nickel

Introduction

Correlating atomic charges with binding energies from X-ray photoelectron spectroscopy data has been the topic of many recent publications. It was our objective to use ESCA<sup>1</sup> to show the correlation between Ni 3p and 2p<sub>3/2</sub> binding energies and the atomic charge on nickel in a number of compounds. The series of compounds examined consisted of nickel carboranes and more common nickel coordination compounds.

### Experimental

A total of 14 nickel compounds were included in this study, of which 7 were nickel carboranes. Compounds 2 through 8 listed in Table I were provided by A. R. Siedle of the University of Indiana; compound 1 was provided by Professor M. F. Hawthorne of the University of California at Los Angeles. Nickel(II) chloride hexahydrate was a commercially prepared sample (Baker and Adamson Reagent grade). Tris-ethylene-diamine nickel(II) thiosulfate,<sup>2</sup> potassium tetracyanonickelate(II) monohydrate,<sup>3</sup> and potassium tris-(aminoacidato) nickel(II),<sup>4</sup> and potassium nickel(IV) paraperiodate 0.5 hydrate<sup>5</sup> were prepared by standard synthetic methods. The instrument used in this study was the iron-free X-ray photoelectron spectrometer developed at the Lawrence Berkeley Laboratory.<sup>6</sup> An aluminum anode was used as the X-ray excitation source. The samples were thoroughly ground into a fine powder before brushing onto a copper tape which was mounted onto sample holders.<sup>7</sup> Sometimes the grinding and mounting was done in a dry bag to prevent prolonged exposure to air. To minimize charging effects, the samples were referenced against gold. A small reproducible amount of gold,  $2 \times 10^{-4}$  mg/cm<sup>2</sup>, was vacuum deposited on one of two samples. The gold was cut from calibrated 0.002 in. diameter wire of 99.9% purity. The following is a discussion of the exact weight of gold deposited per unit area. Considering the gold mass, M (0.2 mg), to be concentrated at the point 0, the amount of gold, m, deposited on the target, a circle of radius r (0.5 cm), with its center at a distance d (10 cm) from 0, is equal to the amount that would have been deposited on the curved surface of the spherical zone determined by the intersection of the plane of the target

with a hemisphere of radius  $R$  and center  $O$ . This area is given by  $2\pi Rh$ , where  $h$ , the height of the zone is equal to  $R - d$ . The amount of gold deposited on any area of the hemisphere is equal to the original gold mass times the fraction of the total area of the hemisphere being considered. This yields:

$$m = M \cdot \frac{A}{2\pi R^2} = \frac{M2\pi(\sqrt{d^2 + r^2})(\sqrt{d^2 + r^2} - d)}{2\pi(d^2 + r^2)} = M \left(1 - \frac{d}{\sqrt{d^2 + r^2}}\right)$$

Since this is the amount of gold deposited on the circle of radius  $r$ , dividing this by the area of the circle will give deposition in terms of  $\text{mg}/\text{cm}^2$ .

When the spectra were recorded, the sample with gold deposited on the surface and the other sample were run in succession. First the spectra for gold  $4f_{7/2}$  and  $4f_{5/2}$  peaks and the peak of another element in the compound were recorded, e.g., the boron  $1s$  peak in the carboranes. Then, the sample without gold was scanned for the nickel  $3p$  and  $2p_{3/2}$  peaks and the other element peak. This type of internal standard referencing against gold was necessary because the intensity of the nickel peaks is weak and vacuum deposition of gold increased the background count sufficiently to obscure entirely the peaks of interest. The influence of gold deposition on the background counts is clearly seen in the iodine data. The iodine  $3d_{5/2}$  peak in  $\text{KNiIO}_6 \cdot 0.5\text{H}_2\text{O}$  without gold deposition after 20 scans has a peak-to-background ratio of 83,000:52,000. A gold layer decreases the ratio to 44,000:35,000 after 12 scans. The total counts are, of course, different since the sample without gold was scanned an additional eight times. However, the ratio changes from approximately 1.6 without gold to 1.3 with gold.



This decrease is due to the increase in background count with gold deposition. All references were made with respect to the gold  $4f_{7/2}$  binding energy of 84.0 eV.<sup>8</sup>

### Results

Originally the peaks were referenced against the carbon 1s peak arising from the spectrometer pump oil. The values obtained were not reproducible for several reasons. The composition of the pump oil vapors is not known and could easily vary from run to run. Also, the deposited oil need not be in electrical equilibrium with the sample.<sup>9</sup> In addition, many of the compounds examined contained carbon and contributed to reference peak broadening since more than one type of carbon was present.

The binding energies listed in Table I were obtained by measuring the spectrometer current at the peak maximum, converting this current to kinetic energy, determining the chemical shift between the peak of interest and the reference gold  $4f_{7/2}$  peak, and finally determining the binding energy value from an established value for the gold  $4f_{7/2}$  binding energy. The table used to convert spectrometer current to kinetic energy was developed after the spectrometer constant was established.<sup>10</sup> Since the dimensions of the instrument and sample positioning were maintained, we did not feel recalibration was necessary.

In general, the Ni 3p peaks were fairly broad and the given values for peak location could vary as much as  $\pm 0.33$  eV. The Ni  $2p_{3/2}$  peaks were more intense and could be located to  $\pm 0.25$  eV. These error values are equivalent to  $\pm 1$  channel each corresponding to 0.2 ma in the two regions scanned. This large error in peak location is, in part, due to the small atomic percentage of nickel in the compounds, especially in the carboranes ( $\sim 4\%$ ).

Peak resolution was complicated by broadening caused by shake-up transitions and multiplet splitting. Shake-up peaks, which appear as satellites to the principal peak, are the result of multiple excitations occurring simultaneously.<sup>11,12</sup> The major core photoelectron emission is accompanied by valence to conduction band transitions. The energy required for the latter type of transition is supplied by the loss in kinetic energy of the emitted photoelectron. Therefore, these peaks appear on the low kinetic energy side of the parent peak. To assign a specific transition to a given shake-up peak would be difficult, if not impossible, for several reasons including multiplet splitting and the overlapping of energy regions for different transitions. A clear example of the latter is seen in Fig. 2 of Novakov's article.<sup>11</sup>

Multiplet splitting arises from multiplet states which result from a coupling of a core subshell hole with an unfilled valence subshell. Any unpaired valence electron will affect differently core electrons of opposite spins. Parallel spin electrons will experience a non-vanishing exchange interaction which will lead to a variation in average wave function radii. Antiparallel spin electrons will lack this exchange energy. Therefore, the antiparallel electrons should be distinguishable from the parallel spin electrons. Hartree-Fock calculations predict the splitting which should be observed. Most often, the measured splitting is less than that calculated for a free ion. Covalent bonding is thought to be responsible for this reduction.<sup>13</sup>

The above affects are reflected in the large average full width at half maximum of at least 3 eV for Ni 3p and approximately 3 eV for Ni 2p<sub>3/2</sub> peaks. See Figs. 1 and 3 and compare these to the reference

peaks in Figs. 2 and 4. Figure 3 represents our poorest results. The compound is  $K[(1,2-(CH_3)_2B_9C_2H_9)_2Ni]$  without gold deposition. The nickel peaks are very diffuse and show a much larger error than that of other compounds examined. The 3p peak is especially broad and must be assigned an error in peak location of  $\pm 1.5$  eV and the peak's full width at half maximum of approximately 7 eV. The  $2p_{3/2}$  peak shows less broadening with a peak location error of  $\pm 0.75$  eV and a full width at half maximum of 2.5 eV. The reference peaks, Fig. 4, show no such broadening and maxima can be easily pin-pointed.

Of the compounds examined, several were run more than one time, and these are indicated in column 2 of Table I. In these cases, the reported values are averages of at least two runs. The variation in binding energies was never more than the experimental error of  $\pm 0.3$  eV.

In addition to those compounds listed in Table I, several other compounds were investigated:  $Cs(1,2-B_9C_2H_{11})_2Ni$  provided by M. F. Hawthorne and  $Cs_2^+(B_{10}CH_{11})_2Ni$  provided by A. R. Siedle. Unfortunately, the cesium  $4d_{5/2}$  and  $4d_{3/2}$  peaks are very intense. Since they lie at approximately 77 and 79 eV, respectively, the  $K_{\alpha 3,4}$  radiation peaks which lie 10 eV lower interfere with the Ni 3p peaks. We attempted to determine these peaks by locating the cesium peaks in the spectrum of CsCl and subtracting them from the nickel carborane spectra. However, this procedure did not produce spectra which would unequivocally locate the Ni 3p peaks. Therefore, these data have been omitted from the table.

### Discussion

The Ni 3p and  $2p_{3/2}$  binding energies listed in Table I must be divided into two groups, the carboranes and other coordination compounds, to discuss the obtained values. The carborane series, compounds 1-7, show the expected general trend: a higher oxidation state of nickel gives a higher binding energy. However, the data show that these values do not vary as greatly as one might have expected. A strict correlation of binding energy with atomic charge in coordination compounds is valid only in studies involving a metal in various oxidation states with a constant number of similar ligands.<sup>14,15</sup> Nickel in the carborane series does have an almost constant immediate environment of six boron and four carbon atoms, with compound 4 being the only exception (eight borons and two carbons).<sup>16</sup> Not only is nickel bonded to the same atoms in all compounds, the structure of the compounds is nearly constant. Since nickel has a +4 or +3 oxidation state in these compounds, it would correspond to a  $d^6$  or  $d^7$  transition metal. This would lead to a symmetric rather than "slipped" configuration, i.e., the carborane "cages" are located directly above and below the nickel atom instead of being located more toward the boron atoms in both cages. The latter slipped structure results from  $d^8$  or  $d^9$  compounds in which there are more electrons than can be accommodated in the symmetric configuration molecular orbitals.<sup>17,18</sup>

Since the environment is invariant, bonding and charge transfer must be responsible, at least in part, for the small range of binding energies. These compounds consist of a nickel ion between two icosahedral fragments with the metal ion completing the two icosahedra. The bonding faces of

the icosahedra are pentagonal and closely resemble the cyclopentadienyl faces in the metallocene compounds. X-ray crystallography has confirmed the "sandwich" structure of carborane compounds.<sup>18,19,20</sup> Therefore, analogous bonding would principally involve overlap of filled ligand molecular orbitals, M. O.'s, with empty nickel orbitals. Back-bonding from filled nickel orbitals into the empty ligand M. O.'s would enhance bonding, but as pointed out by Cotton,<sup>19</sup> this type of bonding is not essential to the existence of an analogous compound. The overlapping of filled ligand M. O.'s into empty nickel orbitals would produce a less positive nickel than expected from atomic charge considerations and lead to lower than expected binding energies. We believe that this type of electron donation is responsible for the observed data.

The second group of compounds considered, numbers 8-14, are, with the exception of number 14, more traditional coordination compounds. These particular compounds were chosen because they represented nickel in a +1 or +2 oxidation state in cationic and anionic environments and in neutral molecule. The binding energies vary by approximately 2 eV for several reasons. First, the atoms bonded to nickel are different: C, N, O, and Ni. From Pauling electronegativities, one would expect nickel bonded to oxygen to be more positive, i.e., have a higher binding energy, than nickel bonded to carbon with all other conditions held constant. The second and equally important consideration is the nickel coordination number. Six bonded ligands would tend to donate or withdraw electrons

to a greater extent than four bonded ligands of the same kind. The magnitude of gain or loss would, of course, be determined by the ligand. Our data are in general agreement with the above. Nickel coordinated to six oxygens gives larger binding energies than nickel bonded to four nitrogen atoms. Nickel bonded to six nitrogens has the same or slightly lower binding energy than nickel bonded to four nitrogens. Our series is complicated by possible back-bonding in compounds 9 and 14. One would normally expect nickel bonded to four carbons to have lower binding energies than when it bonds to four nitrogens. However, compound 9 clearly shows back-bonding produces a more positive nickel and higher binding energies.

Acknowledgements

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Table I

	Compound	Repeated Runs	Ni Oxidation State	Ni Binding Energies (eV)		Internal Reference	Binding Energy In eV	Structure Reference
				2p <sub>3/2</sub>	3p			
1	(1,2-B <sub>9</sub> C <sub>2</sub> H <sub>11</sub> ) <sub>2</sub> Ni	2	+4	857.4	70.0	B 1s	189.0	18,19
2	(1,2-B <sub>9</sub> C <sub>2</sub> H <sub>11</sub> ) <sub>2</sub> Ni	2	+4	857.0	70.0	B 1s	188.7	18,19
3	1,2-[(CH <sub>3</sub> ) <sub>2</sub> B <sub>9</sub> C <sub>2</sub> H <sub>9</sub> ] <sub>2</sub> Ni		+4	856.6	69.9	B 1s	189.1	18
4	(B <sub>10</sub> H <sub>10</sub> CNH <sub>3</sub> ) <sub>2</sub> Ni		+4	956.5	69.5	B 1s	188.6	22
5	Rb[(1,7-B <sub>9</sub> C <sub>2</sub> H <sub>11</sub> ) <sub>2</sub> Ni]		+3	855.9	69.3	B 1s	188.9	23
6	K[(1,2-(CH <sub>3</sub> ) <sub>2</sub> B <sub>9</sub> C <sub>2</sub> H <sub>9</sub> ) <sub>2</sub> Ni]		+3	955.6	69.3	B 1s	188.9	18
7	K[(1,2-B <sub>9</sub> C <sub>2</sub> H <sub>11</sub> ) <sub>2</sub> Ni]	2	+3	855.6	68.7	B 1s	188.4	18
8	[Ni(H <sub>2</sub> O) <sub>6</sub> ]Cl <sub>2</sub>	2	+2	857.8	69.7	Cl 2s	270.8	21,p.881
9	K <sub>2</sub> [Ni(CN) <sub>4</sub> ]·H <sub>2</sub> O		+2	856.6	69.1	N 1s	398.8	21,p.878
10	K[Ni(gly) <sub>3</sub> ] *		+2	856.5	68.1	O 1s	532.9	24,25
11	KNiIO <sub>6</sub> ·0.5H <sub>2</sub> O ††		+2?	856.0	68.9	I 3d <sub>5/2</sub>	624.2	26
12	Ni[DMG] <sub>2</sub> **		+2	855.6	68.9	N 1s	400.8	21,p.878,886
13	[Ni(en) <sub>3</sub> ]S <sub>2</sub> O <sub>3</sub> †	3	+2	855.6	67.9	N 1s	399.6	21,p.881
14	(C <sub>5</sub> H <sub>5</sub> ) <sub>3</sub> Ni <sub>3</sub> (CO) <sub>2</sub>		+1	855.0	68.5	O 1s	532.4	17,p.692

\* gly = glycinate

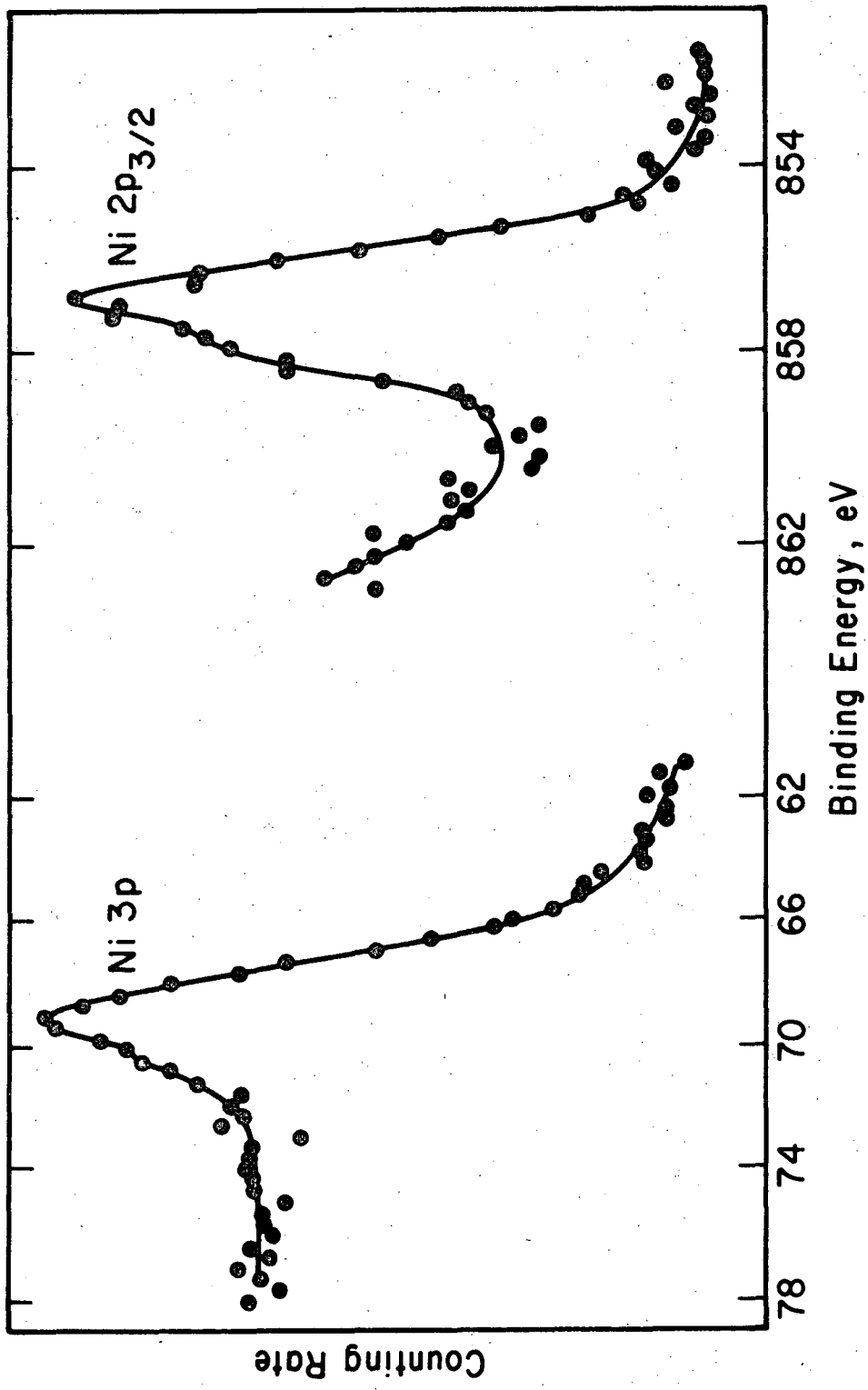
\*\* DMG = dimethylglyoxime

† en = ethylenediamine

†† KNiIO<sub>6</sub>·0.5H<sub>2</sub>O supposedly contains Ni(IV), but in terms of binding energy values and possible shake-up peaks, it would align with Ni(II) compounds. Preliminary magnetic susceptibility studies show the compound to be slightly paramagnetic ( $\mu_{\text{eff}} = 0.79$ ). Additional investigation is required before definite conclusions are drawn.

Figure Captions

- Fig. 1. Nickel 3p and nickel 2p<sub>3/2</sub> spectra for KNiIO<sub>6</sub> · 0.5H<sub>2</sub>O. These are the most well-defined spectra obtained; the total counts for the peaks and low-binding-energy background were approximately 27,000, 21,000 and 64,000, 59,000, respectively. The indicated binding energies are uncorrected; i.e., not referenced to Au 4f<sub>7/2</sub>.
- Fig. 2. Iodine and gold spectra for sputtered KNiIO<sub>6</sub> · 0.5H<sub>2</sub>O. The indicated binding energies are uncorrected.
- Fig. 3. Nickel 3p and nickel 2p<sub>3/2</sub> spectra for K[(1,2-(CH<sub>3</sub>)<sub>2</sub>B<sub>9</sub>C<sub>2</sub>H<sub>9</sub>)<sub>2</sub>Ni]. These are the most poorly-defined spectra obtained; the total counts for the peaks and low-binding-energy background were approximately 4700, 4300 and 9000, 8100, respectively. The indicated binding energies are uncorrected, i.e., not referenced to Au 4f<sub>7/2</sub>.
- Fig. 4. Boron and gold spectra for sputtered K[(1,2-(CH<sub>3</sub>)<sub>2</sub>B<sub>9</sub>C<sub>2</sub>H<sub>9</sub>)<sub>2</sub>Ni]. The indicated binding energies are uncorrected.



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Fig. 1

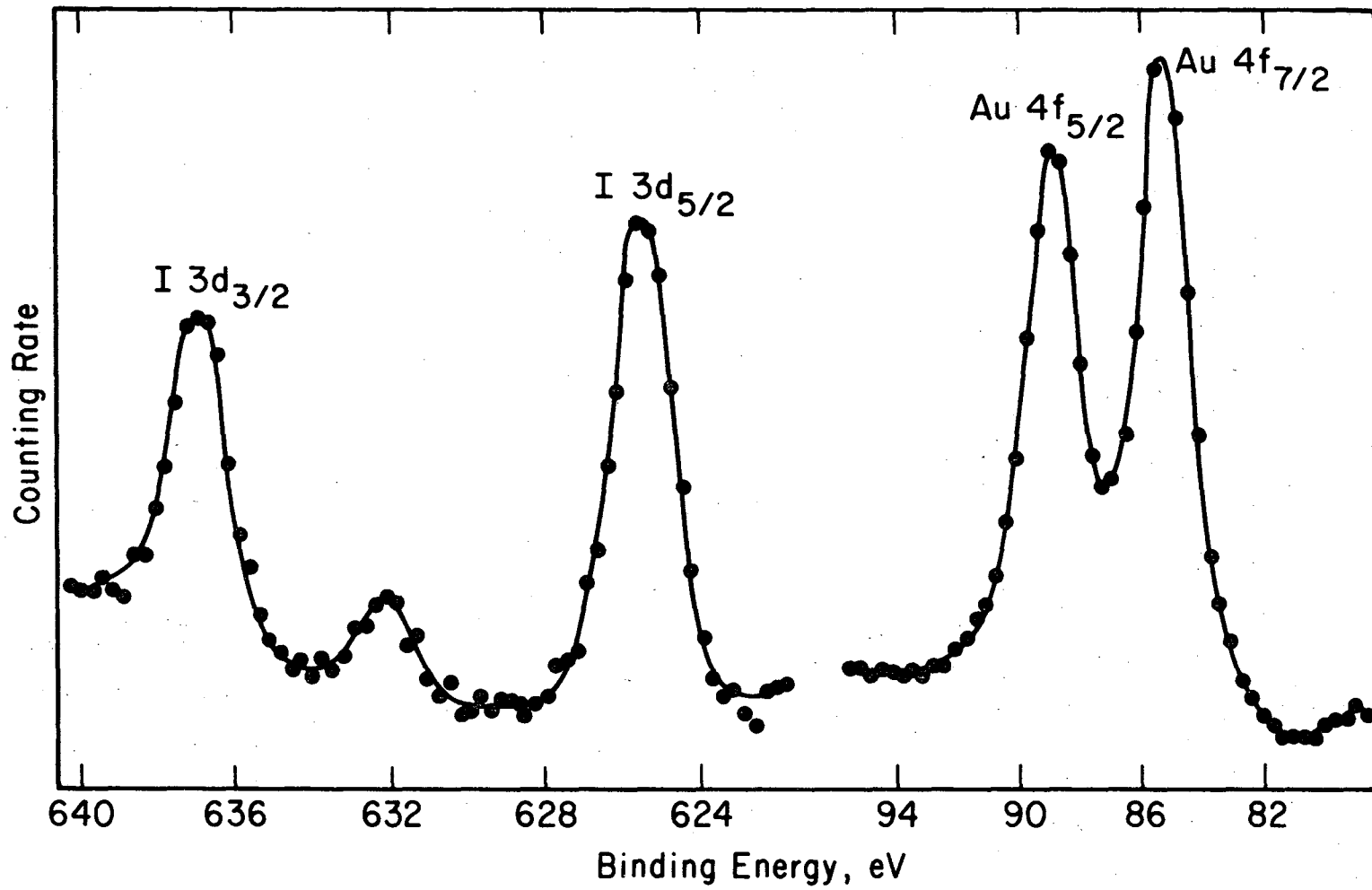
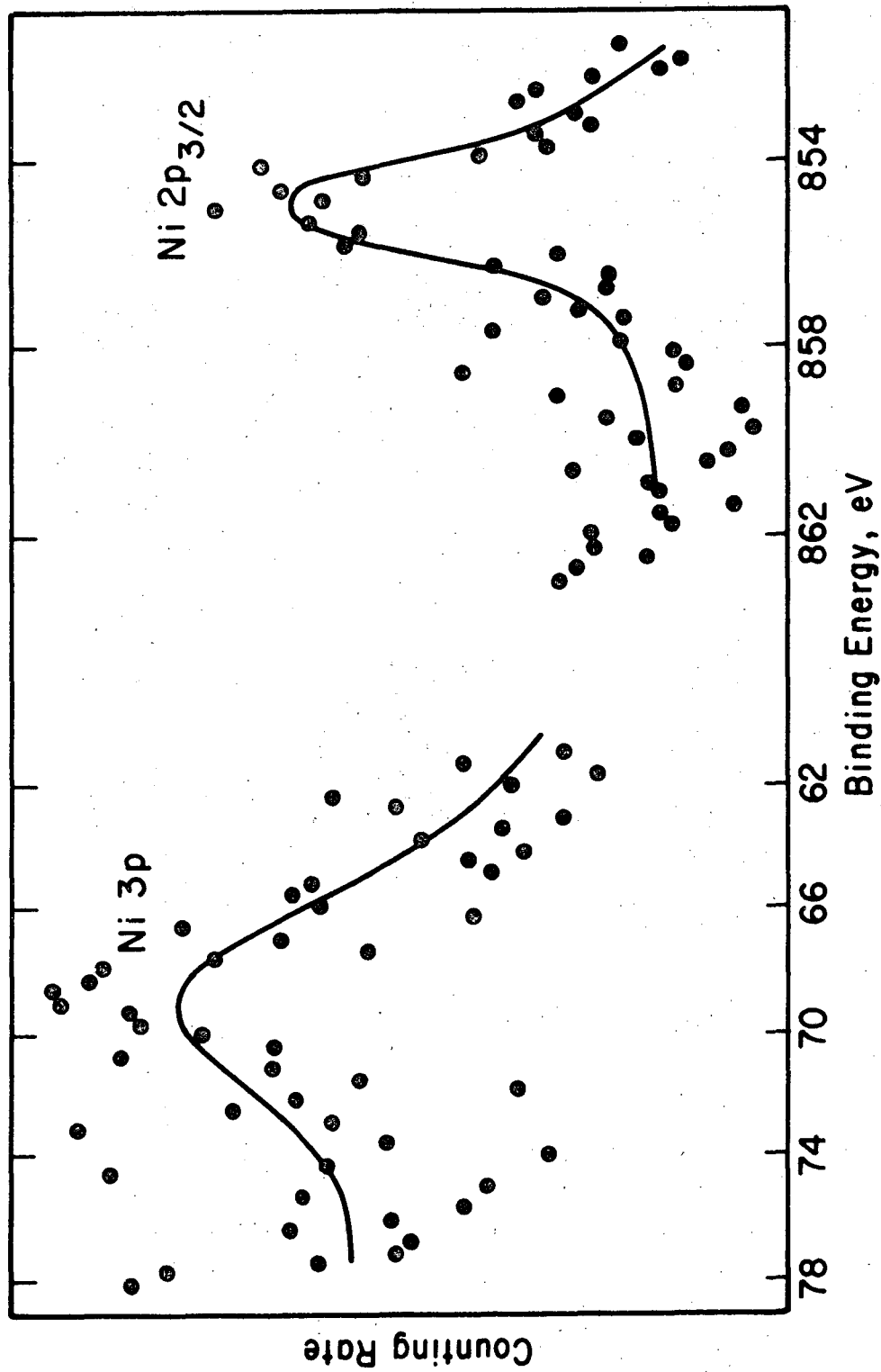


Fig. 2

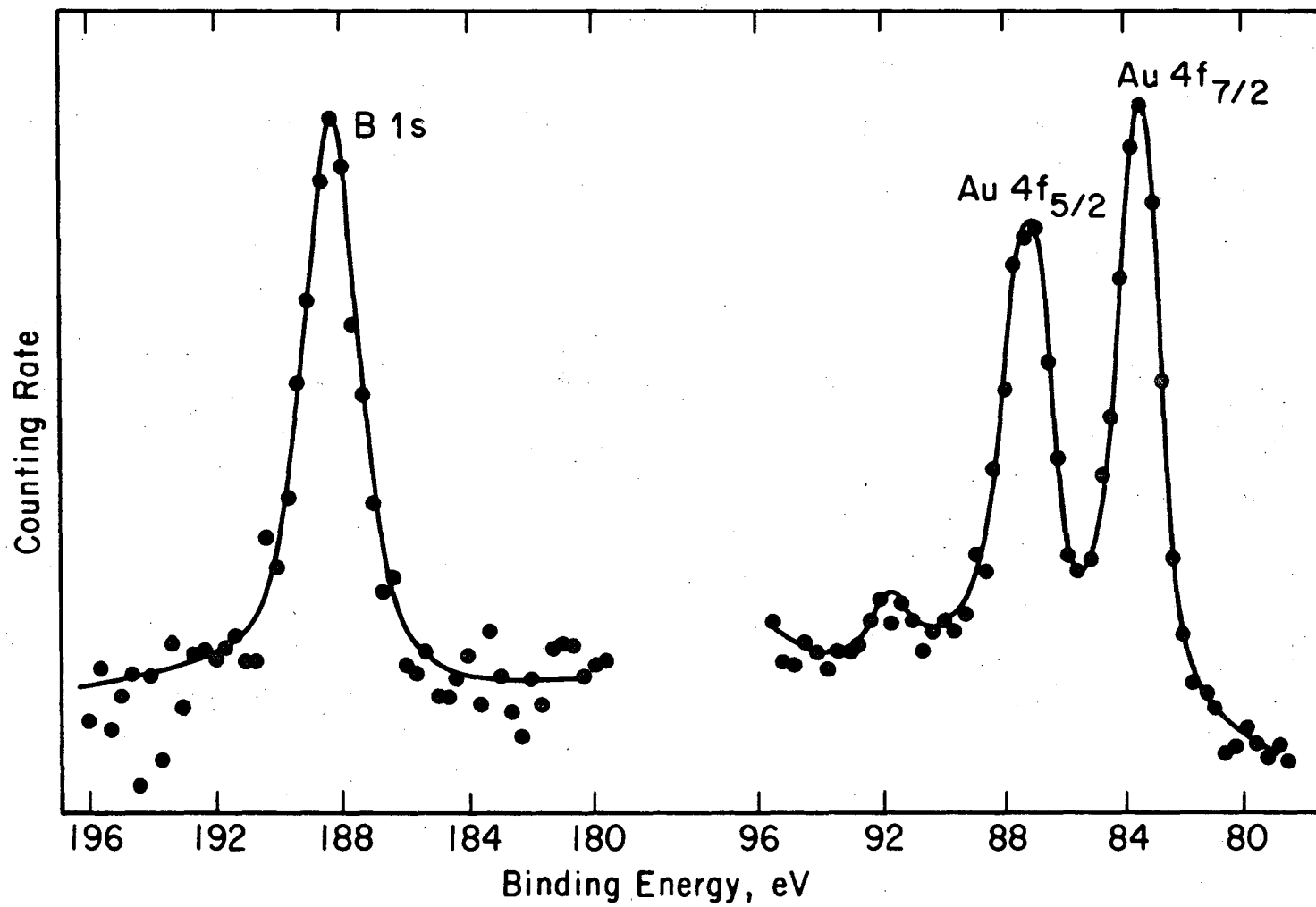
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XBL 735-6089

Fig. 3



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XBL 735-6087

Fig. 4



Paper II. Iron

Introduction

ESCA<sup>1</sup> has been found to be a useful tool in predicting the binding energy of core electrons once an atomic charge is assigned to the atom of interest. Our work was aimed toward clarifying the anomalous behavior observed in various iron compounds. A recent paper by Kramer and Klein<sup>2</sup> lists the 3p binding energy of iron in several inorganic and organic compounds. The binding energy of iron in a +3 oxidation state in  $K_3FeF_6$  is shown as the same as that of iron in a +6 state in  $K_2FeO_4$ . One would have expected iron in the latter compound to have larger binding energies than the former since its atomic charge is double that of  $K_3FeF_6$ . The observed inconsistency may be due to the strong oxidizing power of  $K_2FeO_4$ . A contaminating oxide coating could possibly account for the lower than expected binding energy of iron. Our objective was to establish the 3p and 2p binding energies of several iron compounds in various oxidation states referenced against gold.

Experimental

Six compounds were examined to determine the iron 3p, 2p<sub>3/2</sub> and 2p<sub>1/2</sub> binding energies. Of the compounds listed in Table I, three were commercial samples: Baker's potassium hexacyanoferrate(II) trihydrate, Baker and Adamson's Reagent grade potassium hexacyanoferrate(III), and Baker's ferric oxide. The remaining three were prepared by standard syntheses: zinc tetraoxoferrate(III),<sup>3</sup> magnetite, Fe<sub>3</sub>O<sub>4</sub>,<sup>3</sup> and potassium tetraoxoferrate(VI).<sup>4</sup> The above compounds were studied on the Berkeley iron-free X-ray photoelectron spectrometer<sup>5</sup> using aluminum K<sub>α</sub> radiation. Samples were ground into a fine powder before brushing onto copper tape which was mounted on sample holders.<sup>6</sup> As in an earlier study of nickel compounds, the samples were referenced against gold to minimize charging effects. The small amount of gold,  $2 \times 10^{-4}$  mg/cm<sup>2</sup>, was vacuum deposited on one sample and run against an internal reference, which was another element in the compound. Then the internal reference was run against iron on a sample without gold. Again, this procedure was followed to reference the compounds without obscuring peaks.<sup>7</sup> All binding energies listed in Table I were referenced against the Au 4f<sub>7/2</sub> binding energy of 84.0 eV.<sup>8</sup>

### Results

Binding energies were calculated by measuring the spectrometer current at the peak maxima, converting these into kinetic energy, determining the chemical shift between them and the Au  $4f_{7/2}$  peak, and determining the binding energies from the reference value for the gold peak. These values are listed in Table I along with the elements used as internal references. The spectrometer was not calibrated because the geometric arrangement and dimensions of the instrument were identical to those used in earlier studies.<sup>9</sup>

The use of an internal reference was complicated by the existence of more than a single peak in the case of  $ZnFe_2O_4$  and more so in the case of  $Fe_2O_3$ . Oxygen 1s was used as the internal reference for both compounds. The spectra were complicated by a second peak due to the presence of another oxygen containing species, and one can only speculate on the identity of this contaminant or contaminants. Since no special precautions were taken in handling the sample from the time it was deposited with gold, and from then until the time it was actually run (usually all within 24 hours), the sample had ample opportunity to adsorb water or oxygen from the air. These contaminants would give rise to an oxygen peak at higher binding energy than the oxide oxygen. Comparing the O 1s peak in Figs. 3 and 1 shows first, more than one peak is presented and second, the peak intensities are inverted. This inversion is due to oxygen containing contaminants on the original sample and on the deposited gold. The lower binding energy peak was always used as the reference.

The oxygen spectrum of gold-deposited  $\text{Fe}_2\text{O}_3$  shows a possible third peak. This could be explained by an adsorbed layer of  $\text{O}_2$  on the gold which is at a different potential than either the original contaminant or the oxide oxygen.<sup>10</sup> This would account for the slight shoulder on the high binding energy peak and the entire envelope's large intensity compared to the oxide oxygen. In this case the lowest binding energy peak was chosen for referencing. Positive identification of this peak as the oxide peak would require additional runs comparing the attenuation of sample peaks with that of the sample peaks in a gold-deposited sample. Since a similar problem occurred in  $\text{K}_2\text{FeO}_4$ , this compound was referenced against the  $\text{K } 2p_{3/2}$  peak.

The peaks were broad and peak location was complicated by several factors. Shake-up peaks,<sup>11,12</sup> similar to those appearing in nickel compounds, and multiplet splitting<sup>13</sup> were at least in part responsible for the broadening. Since these topics have been dealt with in detail before, no further elaboration will be made here. The Fe 3p peak could be located to  $\pm 0.3$  eV and the Fe 2p's to  $\pm 0.5$  eV. These error values correspond to  $\pm 1$  and  $\pm 2$  channels in the two different regions scanned. The peaks' full widths at half maximum cannot be determined with accuracy due to broadening by multiplet splitting and interfering shake-up peaks. See Figs. 1 through 3 for representative spectra.

In addition to those compounds listed in Table I,  $\text{Fe}(\text{o-phen})_3(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$  was studied. Due to the extremely low atomic percentage of iron in this compound, approximately 2%, peaks could not be located with any certainty. Therefore, these data were not included.

### Discussion

The data in Table I show the expected trend of higher oxidation states leading to higher binding energies. However, we expected the Fe +6 in  $K_2FeO_4$  to show a higher binding energy. Our value is in exact agreement with that determined by Kramer and Klein, 57.7 eV. We had originally anticipated a larger shift, but our assumptions did not take into consideration the effects of ligands attached to the iron. A comparison of Kramer and Klein's  $K_3FeF_6$  data containing iron in a +3 oxidation state with that for the +6 iron in  $K_2FeO_4$  shows both to have the same binding energies. However, the number and electronegativities of the legands attached to the iron are not the same in both cases. One would expect six fluorine atoms attached to the metal to effectively raise the iron's binding energy due to the large electronegativity of the legands. Also, six fluorines would certainly be more effective in reducing electron density about the metal than four and undoubtedly more so than four oxygens. Therefore, the results are not very surprising.

The magnetite,  $Fe_3O_4$ , iron 3p spectrum is a complicated envelope containing at least two peaks. A Sunder program deconvoluted the envelope into two peaks: one shake-up peak and the iron 3p peak. Although magnetite contains iron in two different oxidation states, our data did not make a distinction between Fe +2 and Fe +3. This is not surprising when one considers the structure of  $Fe_3O_4$ . Magnetite has an inverse spinel structure with one-half of the Fe +3 and all of the Fe +2 in octahedral sites. At room temperature, electron exchange is rapid making these irons "equivalent".<sup>14</sup> The remaining Fe +3 occupying

tetrahedral sites were not distinguished from the "equivalent" irons because all of the iron are actually Fe +3 with an extra electron in a conduction band.<sup>15</sup> Our results are in agreement with theoretical considerations.

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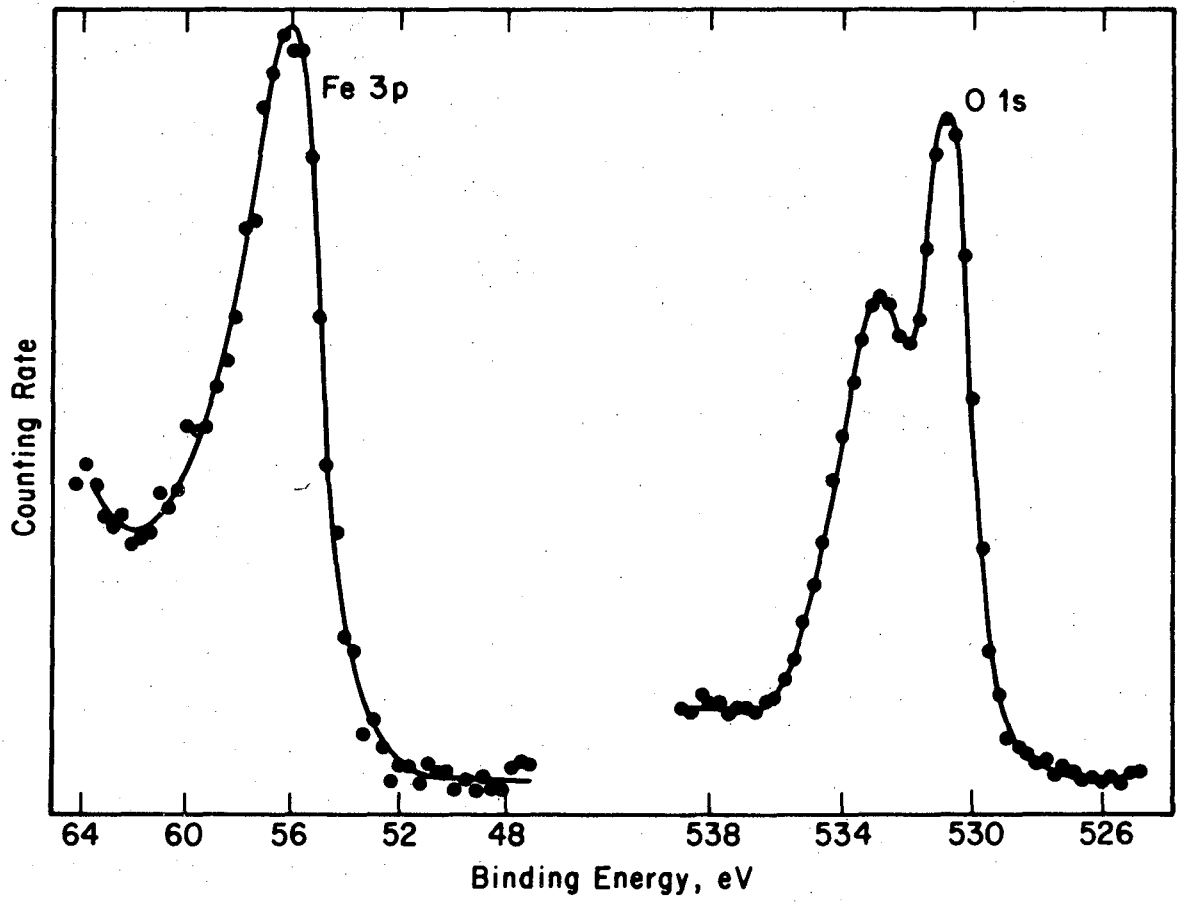
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Table I

Compound	Repeated Runs	Fe Oxidation State	Iron Binding Energies in eV			Internal Reference	Binding Energy In eV
			3p	2p <sub>3/2</sub>	2p <sub>1/2</sub>		
1 $K_4Fe(CN)_6 \cdot 3H_2O$		+2	54.7	709.2	722.0	N 1s	398.1
2 $K_3Fe(CN)_6$		+3	55.5	709.9	723.5	N 1s	397.7
3 $ZnFe_2O_4$		+3	56.3	712.8	726.7	O 1s	530.6
4 $Fe_3O_4$		+2,+3	55.8	711.1	724.3	O 1s	532.3
5 $Fe_2O_3$	2	+3	55.4	711.1	725.0	O 1s	<b>530.2</b>
6 $K_2FeO_4$		+6	57.7	713.1	726.5	K 2p <sub>3/2</sub>	293.0

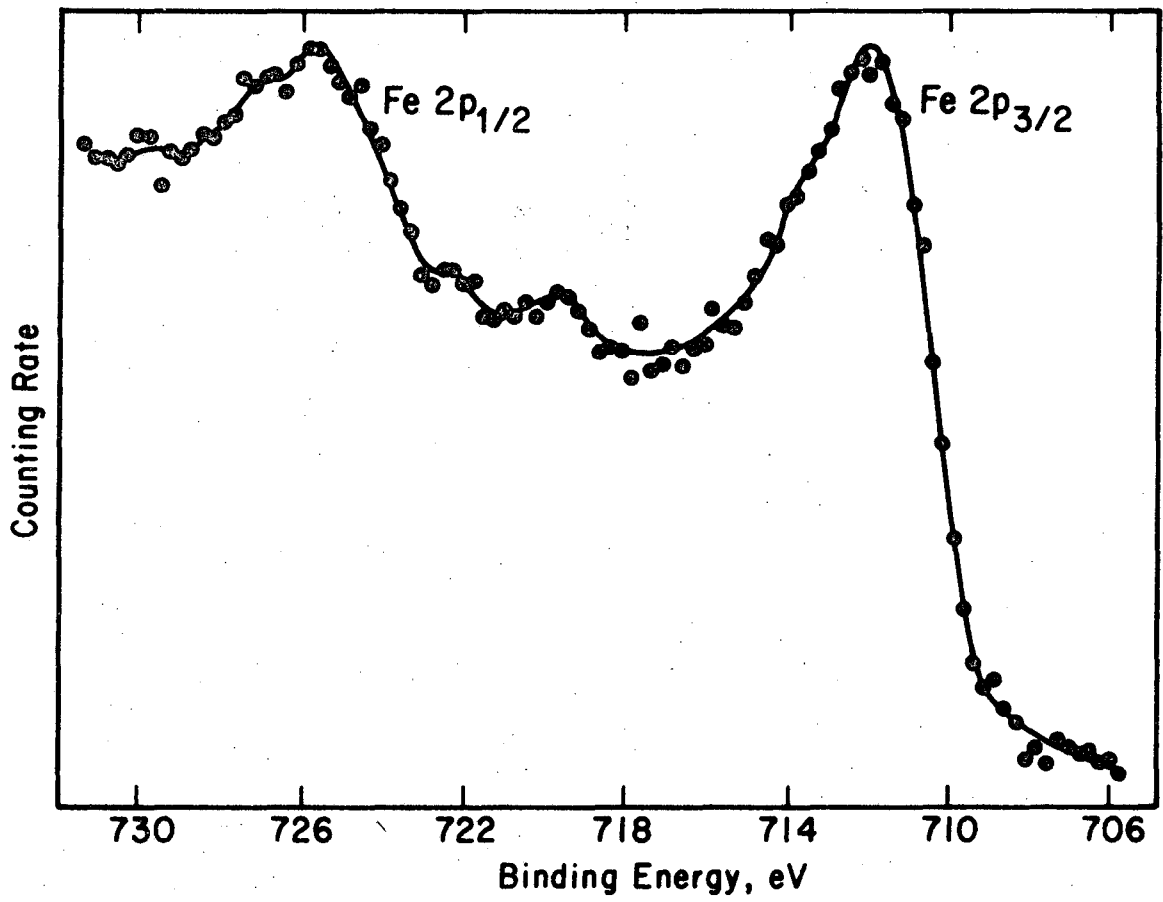
Figure Captions

- Fig. 1. Iron 3p and O 1s spectra for  $\text{Fe}_2\text{O}_3$ . These are representative of the spectra obtained. The Fe 3p total peak counts and low-binding-energy background counts are approximately 9900 and 5800 respectively. The indicated binding energies are uncorrected; i.e., not referenced to Au  $4f_{7/2}$ .
- Fig. 2. Iron  $2p_{1/2}$  and  $2p_{3/2}$  spectrum for  $\text{Fe}_2\text{O}_3$ . The total peak counts and low-binding-energy background counts are 21,000, 14,000 and 21,000, 14,000, respectively. The indicated binding energies are uncorrected.
- Fig. 3. Gold and Oxygen spectra for sputtered  $\text{Fe}_2\text{O}_3$ . The indicated binding energies are uncorrected.



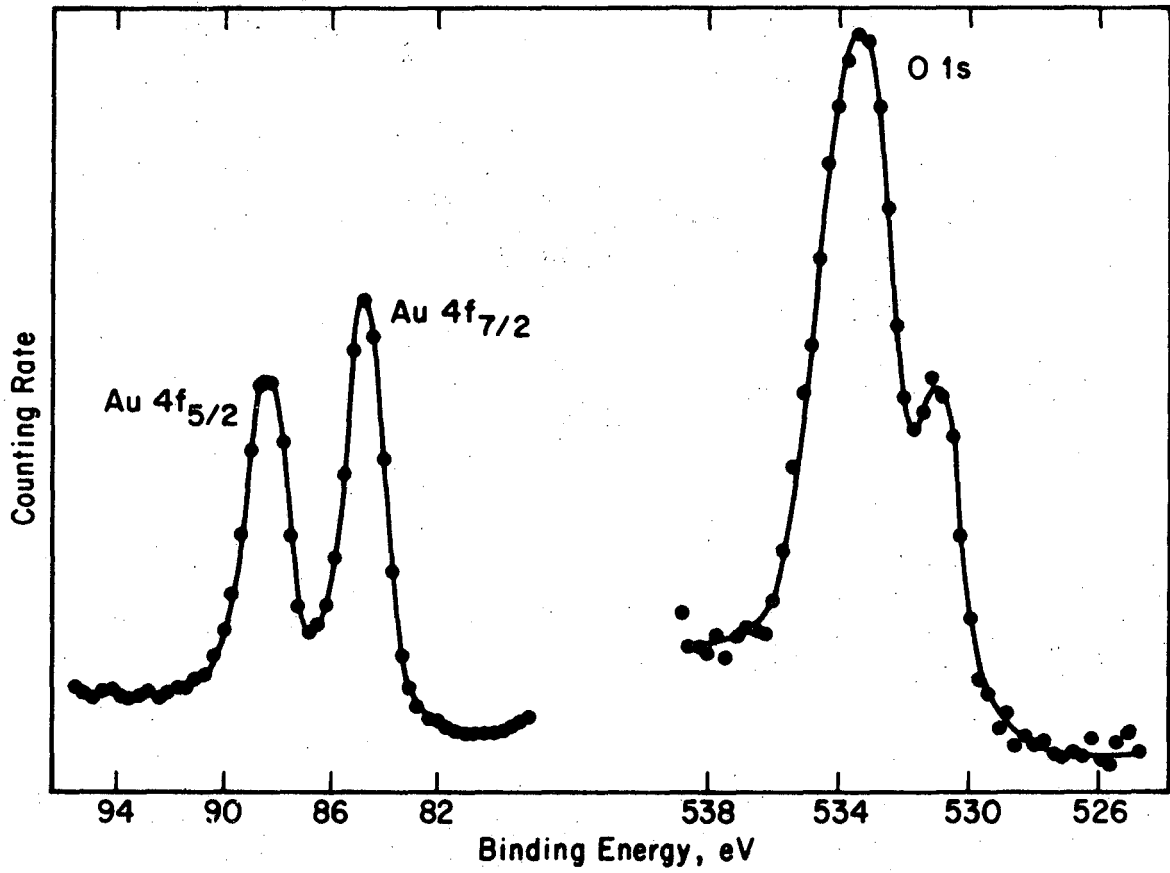
XBL 735-6088

Fig. 1



XBL 735-6091

Fig. 2



XBL 735-6086

Fig. 3

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