$K\alpha$ satellites of Ti, V, Fe, and Co

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Analysis of the x-ray emission spectra of Ti, V, Fe, and Co reveals the existence of new satellites in agreement with the recent results of nonrelativistic Hartree-Fock calculations. Theoretical and experimental values of the energy and relative intensity of these satellites are presented and discussed. Contrary to previous speculations, contributions to satellite spectra due to $2s$ spectator holes, although not appreciable, seem to be significant; they help explain certain features which may not be understood on the basis of $(1s2p)^{-1}\rightarrow(2p)^{-2}$ transitions alone.

I. INTRODUCTION

The presence of weak emission lines on the high-energy side of strong diagram lines of transition elements was first reported by Siegbahn and Stenström.[1] Because of their low intensity and their positions relative to the strong $K\alpha$ lines, they were referred to as satellites and were assumed to originate when a transition occurs in an atom having a spectator vacancy.[2] Based on this hypothesis, several attempts were made to explain x-ray satellite lines,[3–7] but all were met with only limited success. The time-honored work of Parratt,[8] who studied the $K\alpha$ satellites of sulfur and all the elements with atomic numbers between $19\leq Z\leq 32$, was used by most theoreticians to test the results of their calculations.

Most recently, Kuhn and Scott[9] reexamined the problem using nonrelativistic Hartree-Fock calculations and the FORTRAN code of Froese Fischer,[10] in the intermediate-coupling scheme. Possibly, most of the significant relativistic effects in the calculated energies of the transitions are accounted for by using the experimental values of the $K\alpha$ energies, and the spin-orbit parameter $\zeta(2p^{-1})$. These calculations agreed with the relativistic Dirac-Fock calculations performed by Hodge which gave 6427 eV as the configuration average transition energy for the $(1s2p)^{-1}\rightarrow(2p)^{-2}$ transition in iron. When the results of these Hartree-Fock calculations are compared with Parratt's experimental values, points of agreement are readily observed; but there are discrepancies that warrant rechecking the experimental values. For example, in the energy range between 10 and 50 eV above the $K\alpha_1$ line of the element, Parratt reported the existence of five satellite lines while Kuhn and Scott predicted the existence of at least ten for a $2p$ spectator hole alone.

II. EXPERIMENTAL PROCEDURE

The experimental procedure is that which is traditionally used in the analysis of x-ray emission spectra (Fig. 1), but this setup is completely automated. Once the energy and beam current are selected, data acquisition in successive channels corresponding to Bragg's positions is electronically controlled. The target face is set normal to the incident collimated electron beam and in the same plane as the face of the diffraction crystal when $\theta=0$. This arrangement significantly improves the resolution of the system, as the target face acts as an additional slit. In this energy range, $dE/E\simeq 10^{-4}$.

A complete description of experimental procedures has already been published.[11] Data collected as number of counts for a given Bragg's position can readily be converted and presented as a function of energy

$$E=\frac{hc}{\lambda}=\frac{12\,398.13}{2d\sin\theta}\ (\text{eV})\ ,$$

where the crystal constant $d=3.035\,835$ Å and θ is the Bragg angle. The Bragg's positions were taken as $\Delta(2\theta)=5\times 10^{-3}$ deg whose energy value varies from about 0.4 eV/step in the case of Ti to about 1 eV/step for Co.

This investigation was carried out to check on the most recent theoretical predictions, and to resolve the discrepancy between the calculated[9] and measured[8] energy values of the satellites of Ti. Also the possibility of detecting the satellites generated by the transitions $k,[^1P_1\rightarrow{}^3P_1]$ and $l,[^1P_1\rightarrow{}^3P_2]$ is very interesting and significant. These satellites were not reported by Parratt, and correspond to transitions forbidden in pure L-S coupling, but allowed with low probability in intermediate coupling. [The studied transitions are identified in terms of their L-S coupling notations and the same letter designation used in Ref. 9 (Table I).]

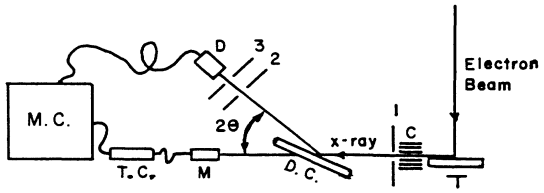

FIG. 1. Schematic diagram of experimental setup, showing from left to right multichannel analyzer (MC), time-selection circuit (TC), stepping motor (M), Na I detector (D), three slits (3,2,1), diffraction crystal (DC), beam collimator (C), and the target (T).

TABLE I. The letters used to identify the studied transitions given in intermediate-coupling notations.

Transitions	Identifying letter
$^3S_1 \rightarrow {}^3P_2$	a^*
$^3S_1 \rightarrow {}^3P_1$	b^*
$^1P_1 \rightarrow {}^1D_2$	a
$^3P_2 \rightarrow {}^3P_2$	b
$^3P_1 \rightarrow {}^3P_2$	c
$^3P_2 \rightarrow {}^3P_1$	d
$^1P_1 \rightarrow {}^1S_0$	e
$^3P_0 \rightarrow {}^3P_1$	f
$^3P_1 \rightarrow {}^3P_0$	g
$^3P_1 \rightarrow {}^3P_1$	h
$^3P_2 \rightarrow {}^1D_2$	i
$^3P_1 \rightarrow {}^1D_2$	j
$^1P_1 \rightarrow {}^3P_1$	k
$^1P_1 \rightarrow {}^3P_2$	l

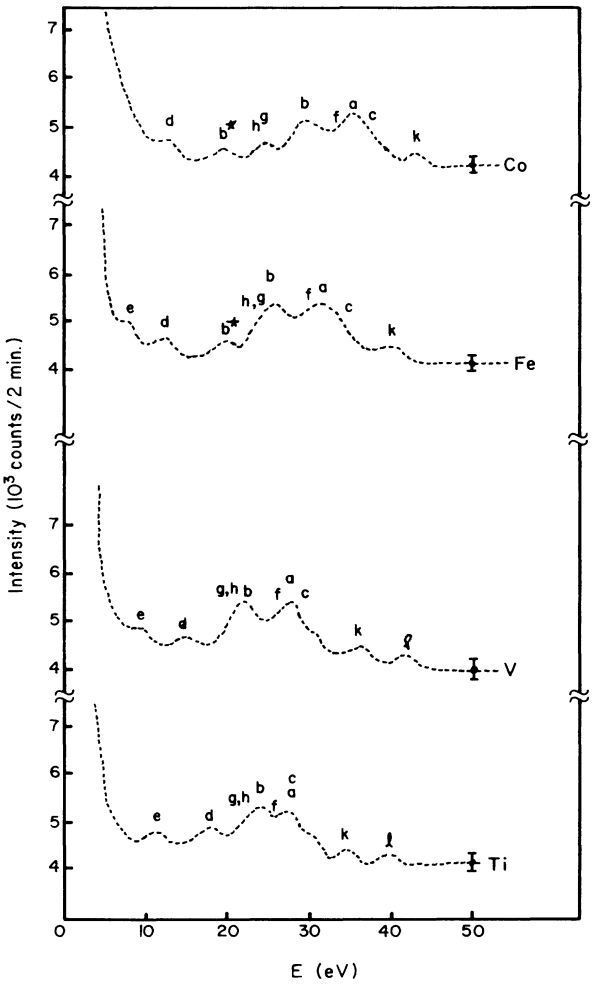

FIG. 2. Observed satellite spectra of the indicated elements, given as a function of energy above the $K\alpha_1$ energy of the element. To reduce statistical uncertainty, the sum of two runs was plotted. The meaning of the identifying letters is given in Table I.

TABLE II. Calculated and observed energy differences $E-E(K\alpha_1)$ in eV of the indicated transitions. (For letter designations, see Table I.)

	Cobalt $[E-E(K\alpha_1)]$ (eV)			
Transition	Theory	Present work	Parratt	
i	8.16		α''	3.3
e	10.17[a]	11.1±1	α'	14.06
j	12.17			
d	16.77	17.4±1	α_3''	19.34
g	20.25			
h	20.78			
b	21.63	23.3±1	α_3	26.46
f	24.22			
c	25.64			
a	26.07	26.8±1	$\alpha_4\alpha_3'$	29.81
k	34.68	33.7±1		
l	39.54	39.6±1		
	Vanadium			
i	7.09		α''	3.22
e	9.71	9.9±1		
j	11.89			
d	16.01	14.5±1	α'	14.40
g	20.54			
h	20.81		α_3''	20.67
b	22.26	27.9±1	α_3	23.97
f	25.32			
c	27.06		α_3'	27.78
a	26.95	28.26±1	α_4	27.25
k	35.87	36.9±1		
l	42.12	42.0±1		
	Iron			
i	5.59			
e	10.00	7.6±1		
j	12.64			
d	15.47	13.9±1		
g	23.92			
h	22.52		α_3''	23.78
b	26.63	26.46±1	α_3	27.14
f	31.06			
c	33.67		α_3'	33.10
a	32.11	32.0±1	α_4	31.09
k	41.99	41.0±1		
b^*	20.34	20.55±1	α'	20.10
	Cobalt			
i	4.19			
e	8.99			
j	11.77			
d	14.23	13.9±1		
g	24.22			
h	21.98	24.5±1	α_3''	24.41
b	27.23	28.25±1	α_3	28.13

TABLE II. (*Continued*).

Transition	Cobalt $[E-E(K\alpha_1)]$ (eV) Theory	Present work		Parratt
f	32.10			
c	34.98		α_3'	34.79
a	32.98	32.98±1	α_4	32.36
k	44.19	43.90±1		
b^*	20.67	19.3±1	α'	20.31

[a]For unresolved groups, the experimental value is on the same line as the most intense component of the group.

III. RESULTS AND DISCUSSION

The satellite spectra of Co, Fe, V, and Ti are shown in Fig. 2, plotted as a function of the energy $[E-E(K\alpha_1)]$; that is, the energy of the $K\alpha_1$ line of the element is the zero of the abscissa. The energy differences between the $K\alpha_1$ line and the satellite structures may then be determined by reading the positions of the peaks. The uncertainty in the numerical values thus obtained is about 1 eV in the case of Co and slightly less for the other elements. These values are given in Table II.

The structure marked e,$[^1P_1 \rightarrow {}^1S_0]$ (Fig. 2) in the spectrum of Fe, V, and Ti, and whose energy separation from the $K\alpha_1$ line decreases with increasing atomic number (Fig. 5), was not reported by Parratt,[8] and we believe it has been observed and identified here for the first time.

The satellite d,$[^3P_2 \rightarrow {}^3P_1]$ is probably that which Parratt designated by the symbols α' in V and α_3'' in Ti. Kuhn and Scott attributed the satellite in both Fe and Co to the h,$[^3P_1 \rightarrow {}^3P_1]$ transition even though the energy agreement is poor. We suggest that it may be the result of a $2s$ spectator hole transition as it corresponds almost exactly to the b^*,$[^3S_1 \rightarrow {}^3P_1]$ transition energy. The assumption that the $2s$ spectator hole does contribute to the satellite spectra helps us understand some intensity results. These were obtained by adding the number of counts under the structure and subtracting the background. The multichannel analyzer has the capability of performing this function. When the incident electron energy is about four times the ionizing energy of the $1s$ electron of the element, the intensity of the fca structure is about 1% of the intensity of the $K\alpha_1$ line.

This work, as well as Parratt's, gives the intensity ratio of the ghb complex to the fca complex, which he designated[8] by $\alpha_3\alpha_3''$, and $\alpha_4\alpha_3'$, respectively, as being almost one, whereas intermediate-coupling calculations give this ratio as being 0.72. This discrepancy can be accounted for

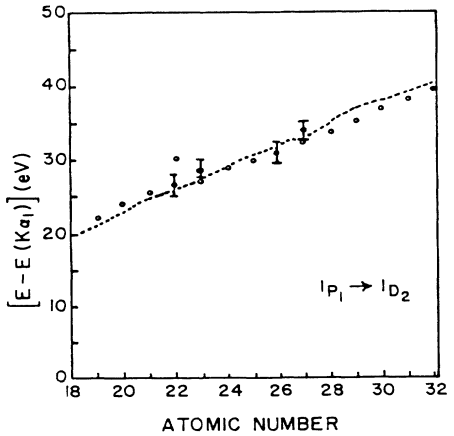

FIG. 3. Experimental and theoretical values of $E-E(K\alpha_1)$ plotted as a function of atomic number for the transition a,$[^1P_1 \rightarrow {}^1D_2]$ [— — —, theory (Ref. 9); ○, Parratt (Ref. 8); ●, present work].

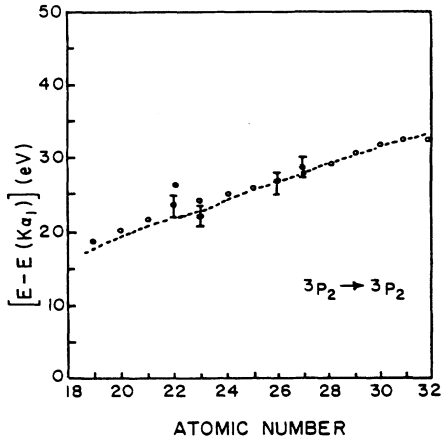

FIG. 4. Experimental and theoretical values of $E-E(K\alpha_1)$ plotted as a function of atomic number for the transition b,$[^3P_2 \rightarrow {}^3P_2]$ [— — —, theory (Ref. 9); ○, Parratt (Ref. 8); ●, present work].

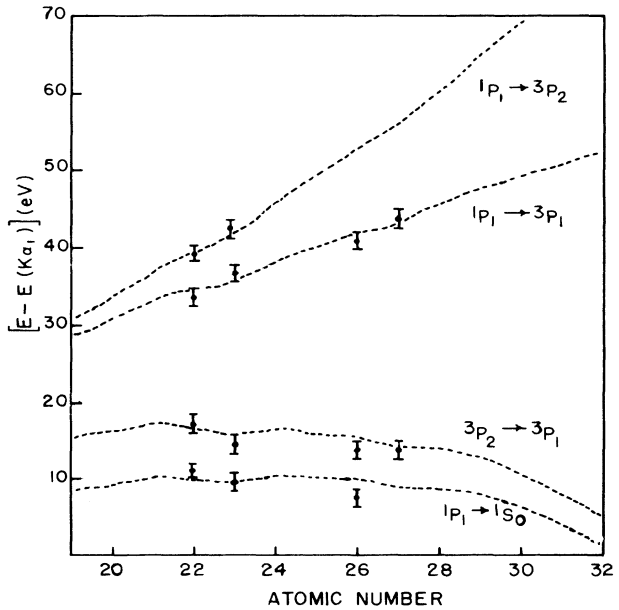

FIG. 5. Experimental and theoretical values of $E-E(K\alpha_1)$ for the indicated transitions, plotted as a function of atomic numbers. [— — —, theory (Ref. 9); ●, present work.]

if one takes into consideration the contribution from $a^*,[^3S_1 \rightarrow {}^3P_2]$, the strongest transition with a $2s$ spectator hole. The energy of a^* is such that it would contribute to the intensity of the ghb group for all elements except Cr and Cu. Our experimental results (Fig. 2) indicate that the intensity ratio $I(b^*)/I(d) \simeq 1.0$, and Hartree-Fock calculations give $I(a^*)/I(b^*)=1.67$ and $I(d)/I(fca)=0.17$; thus $I(a^*)/I(fca)=0.284$; adding this value to that of the $I(ghb)$ complex given $[I(ghb)+I(a^*)]I(fca)=1.00$ in excellent agreement with observations. Transitions with a $2s$ spectator hole are expected to be weak. Various atomic transitions do compete to fill such a vacancy: These include radiative, Auger, and Coster-Kronig. Thus, such a vacancy is expected to have a relatively short mean life reducing the number of satellite transitions requiring its presence. The present results, on the other hand, lead one to believe that although contributions from the transitions $(1s2s)^{-1} \rightarrow (2s2p)^{-1}$ are not large, they are significant.

The satellite lines $k,[^1P_1 \rightarrow {}^3P_1]$ and $l,[^1P_1 \rightarrow {}^3P_2]$ are forbidden in pure L-S coupling, but allowed with low probability in intermediate coupling. They have not been reported in Parratt's work and, to our knowledge, anywhere else. Their observed intensity (Fig. 2) is comparable to that of $e,[^1P_1 \rightarrow {}^1S_0]$.

The numerical values in Table II and the experimental points in Figs. 3–5 were obtained by averaging values of six experimental runs for each element studied. In Table II the calculated and the observed transitions are listed approximately in order of increasing energies above the energy of the $K\alpha_1$ line of the element. Note that in this energy scale the relative position of g and h varies. The satellite line observed at $E-E(K\alpha_1) \simeq 20$ eV in the spectrum of Fe and Co and designated by b^* in this work and by α' in Parratt's is possibly due to a spectator vacancy in the $2s$ state, and its energy value has been moved to the right to indicate that it is not one of the $(1s2p)^{-1} \rightarrow (2p)^{-2}$ transitions.

Figures 3–5 are graphs of the theoretical and experimental values of the energy separation $E-E(K\alpha_1)$ of the studied satellite lines. We reported an estimated error of about 1 eV in the energy position of the satellites, hence the magnitude of the error bars in these graphs. In general, the agreement between experimental and theoretical values is very good. In Figs. 3 and 4, Parratt's results were included for comparison. Agreement is readily observed for all elements except Ti where Parratt's values are some 3–4 eV too high. (Note that Kuhn and Scott[9] had to shift arbitrarily their calculated results by $+4$ eV in order to reach some agreement with Parratt's results.) Our present results for Ti are somewhat lower than Parratt's and are in agreement with the calculated values.

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