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New $K\alpha$ satellites in the electron-excited x-ray emission spectrum of $_{26}$Fe

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A 40-cm curved muscovite mica crystal spectrograph of the transmission (Cauchois) type has been used to identify six new high-frequency $K\alpha$ satellites of Fe at 1.9230, 1.9176, 1.9062, 1.8939, 1.8810, and 1.8698 Å by means of electron excitation. The first four satellites have been assigned to transitions $(1s)^{-1}(2p)^{-n} \to (2p)^{-n-1}$, for $n = 2$–5. Relativistic Dirac-Fock (RDF) calculations for the energies of initial and final configurations give excellent agreement with the experimentally observed energies. However, the last two lines have been only tentatively assigned to transitions $(1s)^{-1}(2s)^{-n}(2p)^{-5} \to (2s)^{-n}(2p)^{-6}$, for $n = 1$ and 2 because RDF calculations for these configurations were were not available. This is the first time that more than two vacancies have been observed following electron bombardment of a target with $Z > 19$. The possibility of such multiple ionization has already been predicted by the well-known shake-off theory. Previously reported results for high-frequency Fe $K\alpha$ satellites have also been recorded. By using the theoretically calculated energies given by Gianturco, the components of the transition $K^{-1}L^{-1} \to L^{-2}$ assigned by Ramberg and Kennard to these satellites under a pure L-S coupling scheme have been confirmed. The satellite α_3'', which does not form a component of the earlier group, has been assigned for the first time to the transition ${}^3P_{1,2} \to {}^1D_2$ allowed in the intermediate-coupling scheme.

I. INTRODUCTION

The occurrence of weak lines (satellites) on the high-frequency side of the prominent diagram lines (parents) in x-ray emission spectra has been known for a long time.[1-7] Since these lines could not be assigned to transitions between any pair of levels of the single-vacancy energy-level diagram, these are also known as nondiagram lines. These nondiagram lines in electron-excited x-ray spectra have been attributed to transitions in atoms with two vacancies in the inner-shells. Most of the reported high-frequency satellites have been explained on this basis.

Recent works[8-14] on x-ray spectra, excited by heavy-ion bombardment, have shown that several inner-shell vacancies are simultaneously created producing numerous high-frequency satellites with greatly enhanced intensity against a considerably reduced background of continuous x-ray spectrum. Since the probability for single ionization is much less, the parent lines appear with sufficiently reduced intensity.

According to the recently published shake-off theory[15-17] for the production of multiple ionization, the probability of production of multiple ionization in inner shells is independent of the mode of excitation, provided the criteria for the validity of the sudden approximation, are fulfilled. Indeed the condition of suddenness will be fulfilled if the time of escape of the K electron outside of the bounds of the L shell is small compared with the periods of the L electrons.[16] This has been amply proved by different workers.[18-20] Graeffe *et al.*[19] in their work on $_{14}$Si illustrate that if the sudden-approximation limit is reached, the $K\alpha$-x-ray spectra produced in primary and secondary excitation reveal similar structures with almost the same intensity ratios.

A reference to the wavelength tables of Cauchois and Hulubei[21] shows that some high-frequency $K\alpha$ satellites in the elements with $11 \leqslant Z \leqslant 19$, could not be attributed to two vacancy transitions. Recent work[8,9] with ionic bombardment establishes that these satellites are due to transitions between atomic configurations involving more than two vacancies. Since these satellites, reported in Cauchois and Hulubei's tables,[21] were the result of electronic excitation, it was thought worthwhile to make an attempt at producing multiple vacancies in atoms by bombarding these by electrons with energies larger than those required by the validity criterion of the shake-off theory. The creation of multiple vacancies will result in the appearance of a number of high-frequency satellites of the kind, reported in ion-excited x-ray spectra, though with far lower intensities.

As part of our program for recording such satellites in electron-excited K-x-ray emission spectra of the elements of the first long period, we report in this paper the results of our investigations in the α region of the K spectrum of $_{26}$Fe. Our measurements were made in a region where the sudden approximation is expected to be valid as the excitation energy was kept approximately more than thrice the threshold energy of the K shell.

In one of the earliest works on the K satellites, Ford[22] reported only one high frequency satellite

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α_3 for $_{26}$Fe. Parratt,[23] reported five $K\alpha$ satellites α', α_3'', α_3, α_4, and α_3'. All these satellites have been associated to single electronic transitions in atoms with two inner-shell vacancies.

Recently, the ion-excited K spectrum of $_{26}$Fe was studied by Burch *et al.*,[24] they used 30-MeV oxygen ions (O^{+5}) as projectiles. They reported two major and two minor components centered at 6437 and 6467 eV and at 6405 and 6500 eV, respectively. Hartree-Fock-Slater (HFS) energy calculations for various L- and M-shell vacancies, over and above the single vacancy in the K shell, justified the assignments. A thorough survey of literature reveals that no satellite corresponding to multiple ionization (more than two vacancies) has been reported in electron-excited K-x-ray spectra of $_{26}$Fe.

II. EXPERIMENTAL PROCEDURE

A metallic hot-cathode demountable x-ray tube (type B-80, supplied by M/S Beaudoin, Paris) with a massive four-faced rotatable anode was used to produce the $_{26}$Fe spectrum. The x-ray tube was evacuated with the help of a continuously running oil diffusion pump (type OD-4) backed by rotary oil pump.

The iron anode was prepared by pressing a disk of spectrographically standardized metallic iron (supplied by M/S Johnson Matthey and Co., London) into a groove cut in the copper target of the x-ray tube. Special care was taken to achieve good thermal contact between the iron disk (thickness of 0.5 mm) and the target base for ensuring efficient heat removal.

The spectrum was recorded on industrial, double-coated x-ray films with the help of a 40-cm curved muscovite mica crystal spectrograph of the transmission (Cauchois) type. First-order reflections from the (100), ($\bar{2}01$), and ($\bar{1}01$) planes of mica were used in the present study. The dispersion achieved was about 0.012 Å/mm in the wavelength region under study.

The x-ray tube was operated at 20–25 kV, 2–4 mA (full-wave rectified). The exposure time ranged from 3 to 30 h. Tb $L\alpha_1$ ($\lambda = 1.9765$ Å)[25] and Ho $L\alpha_1$ ($\lambda = 1.8450$ Å)[25] were used as reference lines for measuring the wavelengths of the satellites.

A Jarrel Ash microphotometer was employed to take microphotometric records of the spectrograms. The wavelengths of the satellites were measured on the microphotograms with the help of an eyepiece (least count of 0.1 mm). The dispersion on microphotograms was about 0.000 85 Å/mm. To reduce statistical fluctuations in the microphotogram data, the different films were scanned several times at different heights and average of measurements, on all such records have been reported.

Wavelength values reported in x-ray units (xu) by earlier workers, have been converted to angstroms (conversion factor 1.002 056 Å/kxu) through out the text.

III. RESULTS

The present investigation has for the first time established the production of multiple inner-shell vacancies following electronic bombardment of $_{26}$Fe. This is revealed by the observation of six new high-frequency $K\alpha$ satellites at 1.9230, 1.9176, 1.9062, 1.8939, 1.8810, and 1.8698 Å. The first four lines have been assigned to transitions in presence of three, four, five, and six inner-shell vacancies, respectively. The nonemperical relativistic Dirac-Fock (RDF) energy calculations[26] for the assigned transitions show good agreement with the experimentally observed energies. However, since such calculations for more than six inner-shell vacancies were not available, the last two lines have been tentatively assigned to configurations with seven and eight inner-shell vacancies. The specific transitions for the newly observed satellites along with the experimental data on the already known satellites are given in Table I. The data of earlier workers are also included for the sake of comparison. The corresponding microphotometric record showing all the reported lines is reproduced in Fig. 1.

Besides the newly observed satellites, the previously reported satellites α', α_3'', α_3, and α_4 have also been recorded in the present study (Table II). However, the satellite α_3' reported by Parratt[23] at $\lambda = 1.9261$ Å could not be resolved in the present work, in view of its close proximity with the satellite α_4 which has been reported by the authors at $\lambda = 1.9266$ Å. All these satellites have been assigned to transitions between atomic configurations with two inner-shell vacancies. The theoretical results of Gianturco[27] in the frozen model have been used to assign transitions to α', α_3, and α_4 allowed in pure L-S coupling scheme whereas α_3'' has been assigned to a transition $^3P_{1,2} \rightarrow {}^1D_2$ allowed in intermediate coupling scheme. Since the satellite α_3'' has been assigned a specific transition for the first time, it was found desirable to test the suitability of this transition in all the elements where this satellite has been reported. Table III gives the data for elements $_{22}$Ti to $_{29}$Cu. The agreement between theory and experiment is excellent, thereby confirming the suitability of transition $^3P_{1,2} \rightarrow {}^1D_2$ for the satellite α_3''.

TABLE I. Data for the high-frequency $K\alpha$ satellites of $_{26}$Fe.

Peak nos. (Fig. 1)	Spectral lines	Wavelength (Å) Ford[a]	Wavelength (Å) Parratt[b]	Wavelength (Å) Authors	Energies (eV) corresponding to present observations	Average energy (eV) observed in present work	RDF energy (eV) for transition[e]	Energy (eV) observed by Burch *et al.*[f]	Transition assigned
1	Tb $L\alpha_1$			1.9765[c]					
2	Fe $K\alpha_2$		1.9400	1.9400	6390.6	6399.4[d]	6400	6399	$(1s)^{-1} \rightarrow (2p)^{-1}$
3	Fe $K\alpha_1$		1.9360	1.9360	6403.8			6405[g]	
4	Fe $K\alpha'$		1.9300	1.9301	6423.4				
5	Fe $K\alpha_3''$		1.9289	1.9291	6426.8	6429.2			
6	Fe $K\alpha_3$	1.9268	1.9279	1.9277	6431.5		6427	6437	$(1s)^{-1}(2p)^{-1} \rightarrow (2p)^{-2}$
7	Fe $K\alpha_4$		1.9267	1.9266	6435.1				
	Fe $K\alpha_3'$		1.9261						
8	New			1.9230	6446.9	6446.9	6446		$(1s)^{-1}(2p)^{-2} \rightarrow (2p)^{-3}$
9	New			1.9176	6465.1	6465.1	6489	6467[h]	$(1s)^{-1}(2p)^{-3} \rightarrow (2p)^{-4}$
10	New			1.9062	6503.8	6503.8	6505	6500[h]	$(1s)^{-1}(2p)^{-4} \rightarrow (2p)^{-5}$
11	New			1.8939	6546.1	6546.1	6554		$(1s)^{-1}(2p)^{-5} \rightarrow (2p)^{-6}$
12	New			1.8810	6591.1	6591.1			$(1s)^{-1}(2s)^{-1}(2p)^{-5} \rightarrow (2s)^{-1}(2p)^{-6}$
13	New			1.8698	6630.3	6630.3			$(1s)^{-1}(2s)^{-2}(2p)^{-5} \rightarrow (2s)^{-2}(2p)^{-6}$
14	Ho $L\alpha_1$			1.8450[c]					

[a] Reference 22 of text.

[b] Reference 23 of text.

[c] Reference wavelengths taken from Ref. 25 of text.

[d] For average double weight is given to Fe $K\alpha_1$ transition.

[e] Bill Hodge (private communication).

[f] Reference 24 of text (ion-excitation work).

[g] This minor component observed by Burch *et al.* is understood to arise due to $(1s)^{-1}(3p)^{-2}$ or $(1s)^{-1}(3p)^{-3}$ initial configuration, Ref. 24 of text.

[h] Burch *et al.* have attributed these to different transitions on the basis of HFS energy calculations, Ref. 24 of text.

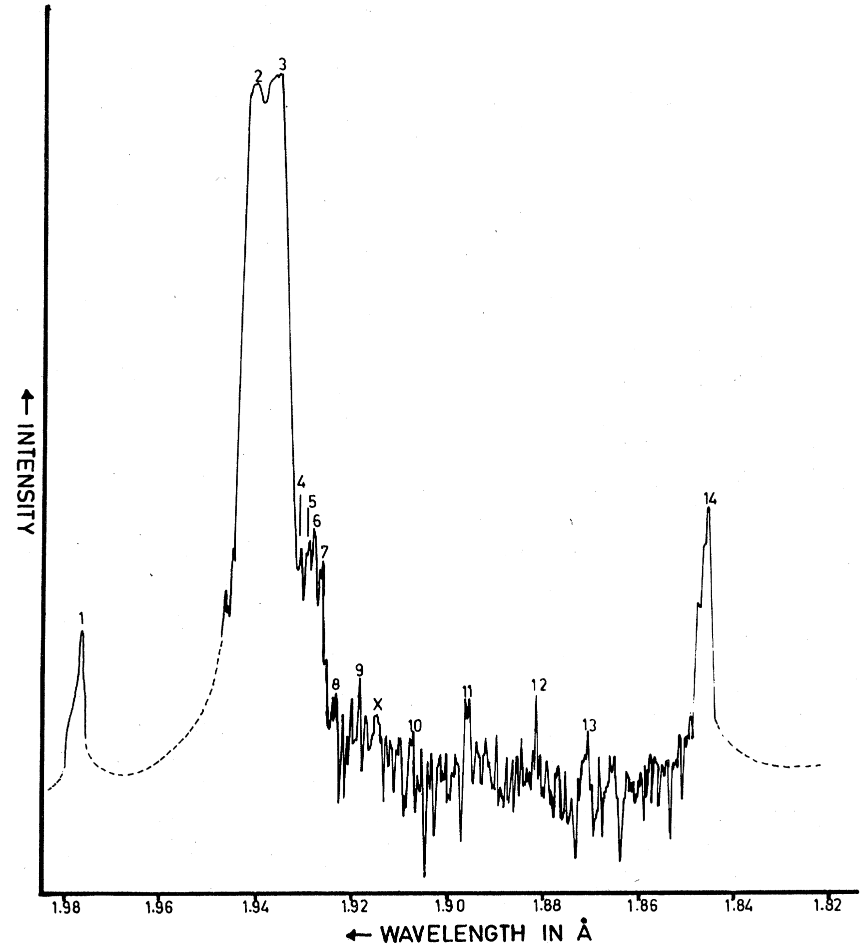

FIG. 1. Microphotometer record of α region of K spectrum of $_{26}$Fe; peaks are labeled (1) Tb $L\alpha_1$, (2–3) Fe $K\alpha_2$ and Fe $K\alpha_1$, (4–7) Fe $K\alpha_{3,4}$ group, (8–13) new satellites, (14) Ho $L\alpha_1$.

IV. DISCUSSION

A. Newly observed high-frequency $K\alpha$ satellites at 1.9230, 1.9176, 1.9062, 1.8939, 1.8810, and 1.8698 Å

This is the first time that in an element with $Z > 19$, more than two vacancies in the inner shells have been produced following electronic bombardment. This possibility has been indicated by the well established shake-off theory.[15-17] This has been concluded by observing for the first time, the six new high-frequency satellites in the electron-excited K spectrum of $_{26}$Fe and assigning them to transitions between configurations involving more than two vacancies.

It is well known that for an atom with atomic number $Z = 26$, relativistic effects can not be taken to be negligible. Further it has also been pointed out by Jundt *et al.*[28] that satellite peak spacings, computed from nonrelativistic HFS theory, depart significantly from experiment with increasing atomic number. It was for these considerations that we decided to use the RDF calculations, involving multiple inner-shell vacancies.

The first satellite observed at $\lambda = 1.9230$ Å has been assigned to the $(1s)^{-1}(2p)^{-2} \rightarrow (2p)^{-3}$ transition. The RDF calculation for the energy of this transition yields the value 6446 eV which is in excellent agreement with the experimentally observed value 6446.9 eV.

The second satellite observed at $\lambda = 1.9176$ Å has been assigned to the $(1s)^{-1}(2p)^{-3} \rightarrow (2p)^{-4}$ transition involving four inner-shell vacancies. Here the experimentally observed energy value 6465.1 eV differs considerably from RDF calculated energy value 6489 eV. This difference in energy may be due to the fact that some high-energy component of this structure could not be registered. However, the satellite component observed at 6467 eV by Burch *et al.*[24] is attributed to transition $(1s)^{-1}(2p)^{-2} \rightarrow (2p)^{-3}$ on the basis of HFS energy calculations.

TABLE II. Transition assignments to previously reported $K\alpha$ satellites of $_{26}$Fe following Gianturco's theoretical energy calculations in "frozen" model.[a]

Transitions allowed in pure *LS* coupling scheme	Transition energy (eV)[a]	Average energy (eV) over triplet states	Present work		Name of satellite
			Observed wavelength (Å)	Corresponding energy (eV)	
$KL_1 \rightarrow L_1L_{2,3}$					
$^1S_0$-$^1P_1$	6423.311	6423.311			α''
$^3S_1$-$^3P_0$	6429.505				
$^3S_1$-$^3P_1$	6434.941	6435.650	1.9261[b]	6436.613	α_3'
$^3S_1$-$^3P_2$	6442.505				
$KL_{2,3} \rightarrow L_{2,3}^2$					
$^1P_1$-$^1S_0$	6423.789	6423.789	1.9301	6423.446	α'
$^3P_1$-$^3P_0$	6437.866	6440.484	1.9277	6431.460	α_3
$^3P_1$-$^3P_2$	6448.582				
$^3P_1$-$^3P_1$	6437.321				
$^3P_0$-$^3P_1$	6444.806				
$^3P_2$-$^3P_1$	6431.806				
$^3P_2$-$^3P_2$	6442.524				
$^1P_1$-$^1D_2$	6445.237	6445.237	1.9266	6435.140	α_4

[a] Reference 27 of text. Relative separation computed by authors have been added to Fe $K\alpha_2$ transition energy (reference wavelength of Fe $K\alpha_2$ taken from Ref. 25 of text).

[b] Observation of Parratt (see Ref. 23 of text).

The third and fourth satellites involving transitions $(1s)^{-1}(2p)^{-4} \rightarrow (2p)^{-5}$ and $(1s)^{-1}(2p)^{-5} \rightarrow (2p)^{-6}$ observed at 6503.8 and 6546.1 eV are in reasonably good agreement with the RDF calculated energy values 6505 and 6554 eV, respectively. Burch *et al.*[24] have observed a satellite component at 6500 eV and is attributed to transition $(1s)^{-1}(2p)^{-3} \rightarrow (2p)^{-4}$ in the light of HFS calculations.

The last two satellites at $\lambda = 1.8810$ and 1.8698 Å could not be conclusively assigned to specific transitions because RDF energy calculations for more than six inner-shell vacancies were not available. However, as the experimentally observed energy is ≈70 and 30 eV below the observed $K\alpha$ hypersatellite energy,[29] we attribute to these two satellites $(1s)^{-1}(2s)^{-1}(2p)^{-5} \rightarrow (2s)^{-1}(2p)^{-6}$ and $(1s)^{-1}(2s)^{-2}(2p)^{-5} \rightarrow (2s)^{-2}(2p)^{-6}$ transitions, respectively. Normally such satellites are not observed because of a fast Coster-Kronig transition filling the $2s$ shell before the x-ray decay occurs, however, if the electrons in the $2p$ shell are missing, one can expect to observe the satellites as here.

B. Previously reported satellites

Parratt[23] was the first to report as many as five $K\alpha$ satellite components of $K\alpha_{1,2}$ in the spectrum of $_{26}$Fe. The first correct identification of these satellites originating from $K^{-1}L^{-1} \rightarrow L^{-2}$ transition was given by Kennard and Ramberg[30] in 1934. This has been supported by recent work of Horák.[31] We have used theoretical results of Gianturco[27] for confirmation of transitions to α', α_3, and α_4 in the *LS* coupling scheme. The match between theory and experiment is fairly good (Table II).

In the present study, the satellite α_3'' has however, been assigned to the transition $^3P_{1,2} \rightarrow {}^1D_2$ allowed in the intermediate-coupling scheme. The agreement between theory and experiment in this case is excellent not only in $_{26}$Fe but in all the elements from $_{22}$Ti to $_{28}$Ni (Table III).

In the end, it will be unjust if we do not make a mention of the peak marked X in Fig. 1, which appears substantially above the background level. In the present study, the existence of this peak was

TABLE III. Transition assignment to α_3'' satellite following theoretical calculations of Gianturco in "frozen" model.[a]

Atomic number Z	Transition allowed in intermediate-coupling scheme	Transition energy (eV)[a]	Average energy (eV) of $^3P_{1,2}$-$^1D_2$ transition	Previously reported work Wavelength (Å)[b]	 Corresponding energy (eV)	ΔE (eV)
22	$^3P_1$-$^1D_2$	4533.975	4532.327	2.7368	4529.950	2.377
	$^3P_2$-$^1D_2$	4530.679				
23	$^3P_1$-$^1D_2$	4975.594	4973.684	2.4929	4973.269	0.415
	$^3P_2$-$^1D_2$	4971.774				
24	$^3P_1$-$^1D_2$	5438.662	5436.365	2.2803	5436.800	−0.435
	$^3P_2$-$^1D_2$	5434.069				
25	$^3P_1$-$^1D_2$	5922.955	5920.279	2.0936	5921.611	−1.332
	$^3P_2$-$^1D_2$	5917.603				
26	$^3P_1$-$^1D_2$	6428.224	6425.194	1.9291[c]	6426.783	−1.589
	$^3P_2$-$^1D_2$	6422.164				
27	$^3P_1$-$^1D_2$	6954.699	6951.335	1.7827	6954.386	−3.051
	$^3P_2$-$^1D_2$	6947.971				
28	$^3P_1$-$^1D_2$	7502.279	7498.597	1.6522	7503.760	−5.163
	$^3P_2$-$^1D_2$	7494.915				
29	$^3P_1$-$^1D_2$	8071.405	8067.316			
	$^3P_2$-$^1D_2$	8063.227				

[a] See Table II (reference wavelength of $K\alpha_2$ is taken from Ref. 25 of text).
[b] Wavelengths taken from Ref. 21 of text.
[c] Value observed in present investigation.

ignored since it was not observed consistently in all our microphotograms.

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