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Outer-Shell Internal Conversion of the 14.4-keV Transition in Fe^{57}: Chemical Effects and Line-Shape Differences

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Internal conversion of the 14.4-keV transition in the outer shells of Fe^{57} following the decay of Co^{57} has been examined at 0.05% momentum resolution. The intensity of the conversion in the outermost shell, N_1 in the free atom, relative to that of the M_1 shell shows a dependence on the chemical environment of the decaying Co^{57} atom. Co^{57} ions from an electromagnetic isotope separator were deposited at <25 eV on the surface ("oxide state") or were allowed at 500 eV to penetrate a natural graphite crystal lattice ("metallic state") where oxidation could not occur. The intensity ratio N_1/M_1 ("oxide") is 0.024 ± 0.002 and N_1/M_1 ("metal") is 0.034 ± 0.003. The N_1-shell line shapes show less low-energy tail than the M_1 lines (which are only ~0.7% lower in energy), an effect probably due to less outer-shell electron shakeoff in the case of the N_1 lines. This result throws doubt on the accuracy of the analyses of previous experiments in which the outermost-shell conversion lines were not well enough resolved to observe this effect and in which the assumption of similar line shapes were used.

INTRODUCTION

The effect of chemical state on the internal conversion probability in the outer (valence) shell has been reported by Bocquet *et al.*[1] They demonstrated a change in the O/N_1 conversion ratio of the 23.87-keV transition in the decay of Sn^{119m} which was correlated with the chemical state (metal vs oxide) of the tin, the oxide having relatively lower conversion in the valence shell than the metal. Another example has been reported by Carlson, Erman, and Fransson (CEF)[2] in which the P_1/O_1 conversion ratio of the 8.4-keV transition in the decay $Er^{169} \to Tm^{169}$ was observed to be a function of the chemical environment of the atom undergoing decay.

We are reporting here a similar effect in the N_1/M_1 conversion ratio in the 14.4-keV transition in Fe^{57m} following the decay of Co^{57}, but in our case the "valence"-shell conversion line is well resolved from other lines, a result not realized in Refs. 1 or 2. The two different chemical states of the parent Co^{57} atoms are achieved by allowing Co^{57} ions (from an electromagnetic isotope separator) to impinge on natural-graphite crystal surfaces with either <25-eV energy or 500-eV energy. The low-energy ions yield sources which give less N_1 (4*s*-shell) conversion relative to M_1 (3*s*) conversion than the sources made with high-energy ions. Just as for the similar M_1 transitions in Sn^{119m} and Tm^{169}, the effect reflects the variation of 4*s*-electron density near the nucleus. We present evidence that the low-energy ions remain on the surface and become oxidized, thus lowering the 4*s*-electron density at the nucleus, whereas the high-energy ions become imbedded in the lattice, retaining a metal-like environment and a relatively higher 4*s*-electron density at the nucleus.

In addition, we find the N_1-shell conversion lines have a markedly different shape than the M_1 (3*s*) conversion lines. In both chemical states the N_1 lines are narrower and have less low-energy tail than the M_1 lines. This is a remarkable result considering that the line shapes being compared are only 100 eV apart at 14 keV and therefore such a result cannot be attributed to energy-dependent extra-original-atom effects.

EXPERIMENTAL DETAILS AND RESULTS

These conversion-electron spectra were observed with the Argonne iron-free toroidal-field magnetic spectrometers[3] operated in tandem. A resolution of 0.052% in momentum (full width at half maximum; measured at the K line of the 122-keV transition) and a measured transmission of 4.5% of 4π is achieved with a 1-mm-diam source and a 1.5-mm-diam final detector aperture. The detector was a bare cleaved-surface thin NaI(Tl) crystal mounted directly on a photomultiplier tube.

Variation in detector efficiency for the very small range in energy over which the M and N line intensities are compared is a negligible effect for the experiment. The discriminator setting gave a background rate of 7 counts/min and a counting efficiency of 72% for the 14-keV electrons.

The source backings were the cleaved surfaces of natural-graphite crystals which were attached with good electrical conductivity to supporting aluminum foils. A 1-mm-diam mask was used in the isotope separator to define the deposit of Co^{57} ions whose energy was controlled by the amount of retardation applied to the separated beam of mass-57 ions. From the total mass-57 current integrated over the collection time one calculates that a mean thickness of less than a monolayer of ions was deposited on the 1-mm-diam area. Nevertheless, in these sources the low-energy lines have greater-than-instrumental width, e.g., ~0.08% at 7.3 keV and 0.06–0.07% at ~14 keV. Source intensities were ~2.5 μCi.

The deposit made with the Co^{57} ions decelerated to essentially zero energy was probably quickly oxidized[4] in the 10^{-5}-Torr pressure of the isotope separator, and certainly on removal to the atmosphere. The 500-eV ions penetrate at least 1 but no more than ~5 atomic planes of graphite, as the calculated minimum kinetic energy needed by a mass-57 ion to displace a carbon atom in a graphite lattice (displacement energy 30–33 eV[5]) is ~55 eV and the maximum energy transfer to a carbon atom is ~280 eV from a 500-eV Co ion. The Co atoms reside interstitially[6] in the lattice in a strongly reducing metal-like environment, but are not chemically bonded as a carbide.

A built-in indicator of the chemical character of the source lies in the energy of the K conversion line of the 14.4-keV transition. The well-known chemical effect on the inner-shell binding energies[7] results in a higher energy for the K conversion line from an atom in a metallic state than from an atom in an oxidized state because the inner-shell binding energies in the oxidized atom are increased as valence electrons are withdrawn, reducing their effective screening of the nuclear charge. Figure 1 shows the 7.29-keV K conversion line of the 14.4-keV transition for each of the sources. Note that the line from the source made with penetrating ions is at a higher energy, not lower as one might expect from a "thicker source," although increased inelastic loss effects are evident in this source in the difference in the shape of the low-energy tail, as expected.

Our studies of a large number of source-backing materials with a variety of source preparations will not be reported here, but we cite the pertinent conclusion from these studies; namely, if the Co^{57} ions are deposited gently on the surface of any solid, the K-line energy is in what we call the "oxide position" and if the ions are placed in a metal or graphite matrix using higher-energy ions or by codeposition of a macroscopic quantity of Fe^{57}, the K line moves to a higher energy position which characterizes the "metallic" state. Both types of sources exhibit the characteristic "metallic" or "oxide" K-line positions immediately after preparation, and neither line position shifts despite months of exposure to the atmosphere. This indicates that the chemical states are stable and that the graphite lattice prevents access of molecular oxygen to the Co despite the radiation damage. The "500-eV" ion sample shows little line component in the oxide position, consis-

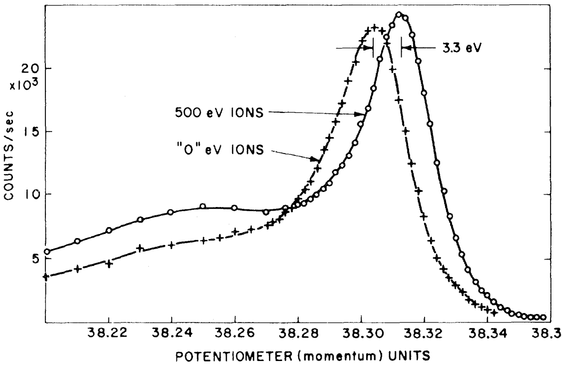

FIG. 1. K internal conversion lines at 7.3 keV from the 14.4-keV transition following the decay of Co^{57}, showing the chemical shift (the change in K-shell binding energy) for sources prepared in different ways. Ions of Co^{57} from an electromagnetic isotope separator were allowed to impinge on natural-graphite crystals at energies of 0–25 or 500 eV. The "0"-energy ions cannot penetrate the graphite lattice and are oxidized on the surface, whereas the 500-eV ions penetrate the lattice and remain in a metal-like environment protected from oxidation. The K-shell binding energy differs by about 3.3 eV in these two chemical states, being lower for the 500-eV ion sample. The sample of buried Co^{57} atoms (500-eV ions) shows, as expected, greater inelastic energy loss by the K conversion electrons as evidenced in the larger fraction of events in the low-energy tail.

tent with the expectation that few of the ions fail to penetrate into the lattice.

We have further evidence which will not be detailed here, based on differences in Mössbauer hyperfine patterns seen[8] on some of our samples, that is consistent with our labeling of the sources as metal or oxide. We can make no definitive assignments, based on any of our evidence, as to which oxidation state(s) we are observing. Also, the relative K-line shifts of the various "metallic" source preparations with respect to the oxide line positions are not sufficiently precise to enable any distinctions to be made between Fe^{57m} in the various "metallic" environments, such as iron, aluminum, or graphite. Thus we are here comparing the change in 4s conversion probability between chemical species which are well defined in terms of the mode of their source preparation, but are not identified precisely with established bulk compounds.

We see from Fig. 1 that the shift in K binding energy is about 3.3 eV for these two chemical states. Source positioning and over-all spectrometer reproducibility contribute an uncertainty of <5% of the shift.

Figure 2 shows the M_1, $M_{2,3}$, and N_1 lines for the

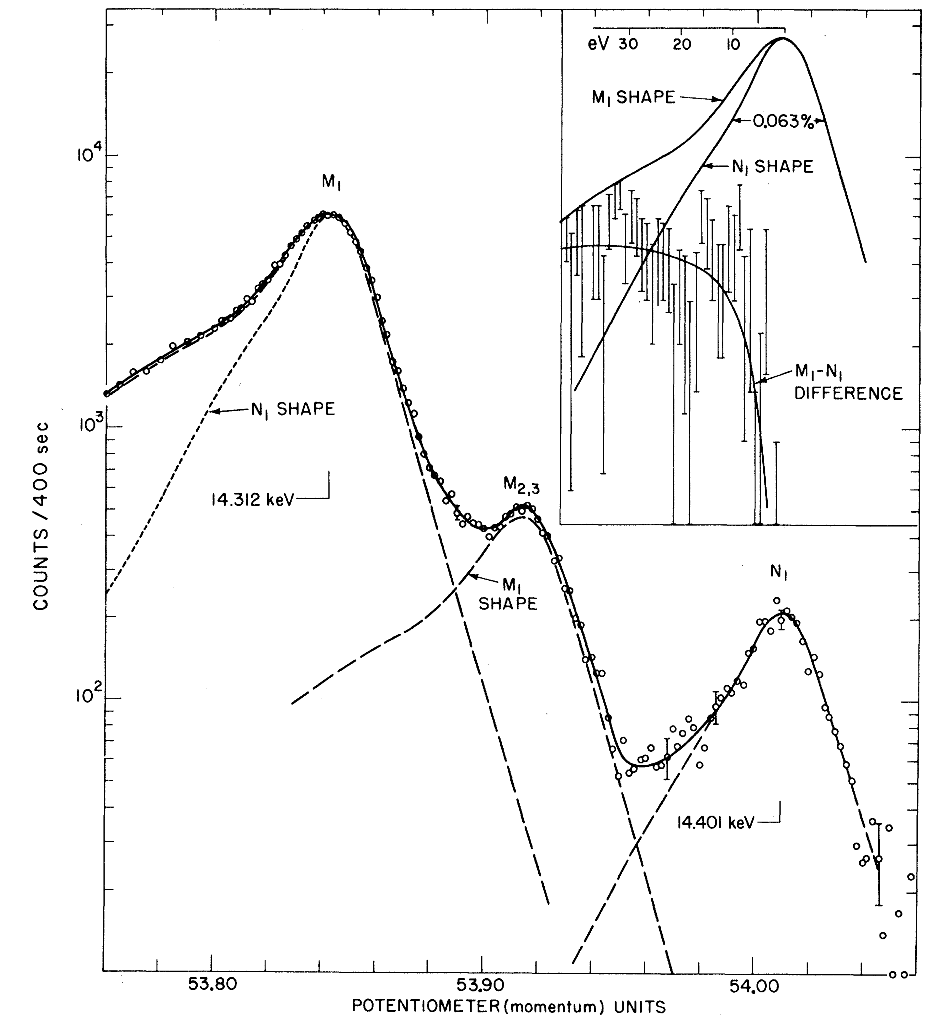

FIG. 2. Outer-shell conversion of the 14.4-keV transition following the decay of Co^{57} from the sample prepared with "0"-eV Co^{57} ions. A constant 58 counts/400 sec has been subtracted from each data point; this background was determined at energies higher than the N_1 line. The longer-dashed curves represent an analysis into the indicated components. Because of the different M_1 and N_1 shapes, areas must be used to obtain the conversion-line intensity ratios rather than peak heights (which could be used if the same shape fitted all lines). The M_1 line area includes the tail extending down ~85 eV below the peak (to 53.68 potentiometer units). The N_1 shape is drawn in (short dashes) at the M_1 line for comparison, matched at the peak- and the high-energy side. In the upper right insert the difference in the shapes is plotted, the error bars being generated by the errors in the tail of the N_1 shape as deduced from the data points. The instrumental resolution measured at the K line of the 122-keV transition is 0.052%.

source made with the "zero"-energy (<25 eV) Co^{57} ions. The line labeled N_1 in principle also contains contributions from the $M_{4,5}$ shells whose binding energy is only slightly (~3 eV)[9] higher than that of the N_1 shell in the free atom. However, the expectation from internal-conversion calculations[10] at $Z=26$ is that the ratio $M_{4,5}/M_{2,3}$ will be $\sim 5\times 10^{-3}$ for the 14-keV $M1$ transition, implying that less than 1% of the observed intensity of the highest-energy line, labeled N_1, will be $M_{4,5}$ contribution (for a free atom).

Figure 3 shows the same lines for the source prepared with 500-eV Co^{57} ions. In each of these figures an analysis into three component lines is given. The shape of the strong M_1 line is evident from the data, and the assumption is made that the $M_{2,3}$ shape is the same. (The M_2-M_3 splitting is probably less than 2 eV, compared to the resolution width of ~15 eV.) With this assumption the N_1 contribution is deduced.

Figure 4 shows the two cases on the same plot where it is easier to see that the peak-rate ratio N_1/M_1 is about 30% smaller for the "zero"-eV ions than for the 500-eV ions.

It is clear from Figs. 2 and 3 that the M_1 line shapes in both sources are different from the N_1 shapes. Therefore, the intensity ratios are obtained more accurately from the area ratios rather than from peak heights (N_1/M_1 area ratios are 30–40% smaller than peak ratios). These ratios,

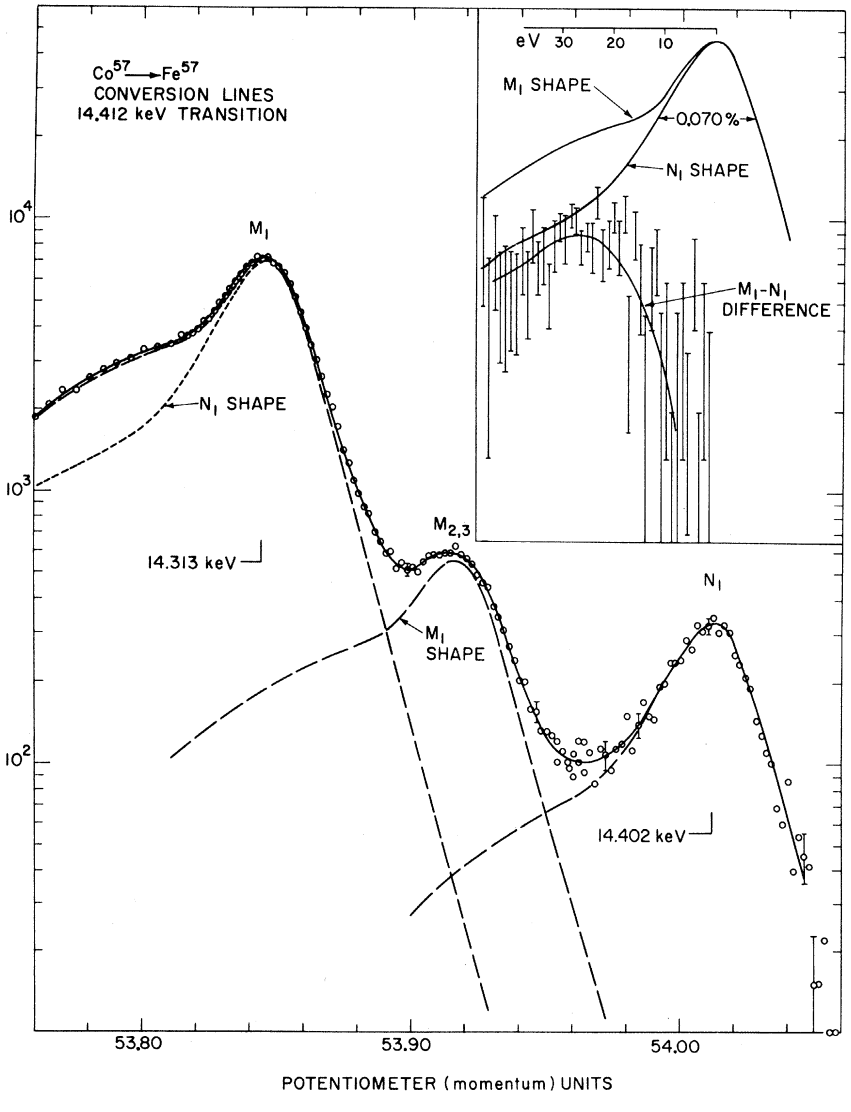

FIG. 3. Outer-shell conversion of the 14.4-keV transition following the decay of Co^{57} from the sample prepared with 500-eV Co^{57} ions. A constant 47 counts/400 sec has been subtracted from each data point. See caption of Fig. 2 for detailed description.

calculated using the analysis indicated by the dashed curves in Figs. 2 and 3, are given in Table I. Here it is seen that the source preparation has little effect on the $M_{2,3}/M_1$ ratio but a large effect on the N_1/M_1 ratio. As was mentioned above, an explanation of the results lies in the different chemical state of the two sources and the attendant difference in outermost-shell electron density at the nucleus, to which the 4*s* conversion probability for a low-energy *M*1 transition should be approximately proportional. We conclude that this density ratio

$$\frac{|\Psi(0)_{4s}|^2_{\text{“metal”}}}{|\Psi(0)_{4s}|^2_{\text{“oxide”}}} = 1.42 \pm 0.21 \; .$$

The assigned error arises largely from the different N_1- and M_1-line tail shapes and tail extrapolations in the two sources, even in these well resolved lines. The ratio of 4*s* conversion probabilities for metal and oxide derived from an erroneous use of the same (M_1) shape fitted at the N_1 peak is 1.30, a 9% difference.

In the succeeding section we present arguments that the gross differences we observe between the conversion-line shapes of valence and inner-shell electrons are to be expected for all atoms, to a significant extent. Therefore, an evaluation of their relative conversion probabilities can only be reliably made in cases where the experimentally realized resolution reveals enough of the full line shape to permit an accurate line-area determination without requiring an extensive unfolding procedure. Even with a resolution good enough to give an N_1 valley-to-peak ratio of ~$\frac{1}{3}$, the uncertain derivation of the N_1 tail resulted in about half of our quoted error of 14%. In both Refs. 1 and 2, the instrumental resolution and source-degradation effects caused the lines to overlap so that there was little or no valley. In such cases, only with the (now unrealistic) assumption of identical line shapes could peak heights be inferred. Thus, one may expect line-intensity ratios in the same sample to be in error (30–40% in our comparison) and even the ratio of the ratios to be in error as noted above for our peak-vs-area determinations.

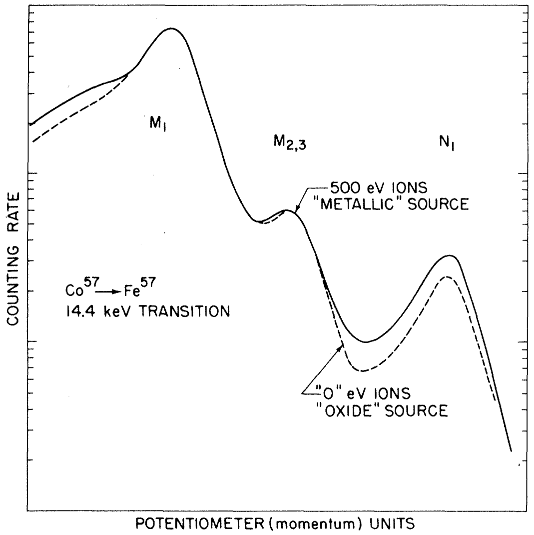

FIG. 4. Outer-shell conversion of the 14.4-keV transition following the decay of Co^{57}. Here the data of Figs. 2 and 3 can be more easily compared by normalizing the curves at the M_1 peak. The chemical effect on the relative intensity of the outermost-electron (“N_1”) conversion line is clear. The “oxide” source exhibits less conversion in the 4*s* (N_1) shell consistent with the expectation that the daughter Fe^{57} valence electrons will have mean displacements farther from the nucleus compared to the metallic case.

The fractional change in the N_1 conversion coefficient (Table I) for the chemical states in Fe is about the same magnitude as observed by Bocquet *et al.*[1] for the *O* shell of tin as oxide and metal and by CEF[2] for Tm^{169} in metallic or oxidizing environments. No theoretical estimates for N_1 conversion are available for Fe. We have included in Table I the Carroll and O'Connell[10] theoretical M_{23}/M_1 ratio which is supported by the experimental ratio. For completeness, Table II lists other relative conversion line intensities for the 14.4-keV transition from our work and that of Ewan, Graham, and Geiger.[11] Our uncertainties lie mainly in the extent of low-energy tails and in detector relative-efficiency corrections over the range 7–14 keV. Table III compares the ratio of total to *K* internal conversion for this transition. All these comparisons show no significant disagreements.

In Table IV are summarized some energy data for the M_1 and N_1 lines of the 14.4-keV transition. Spectrometer calibration was obtained from the *K* conversion line of the 122-keV transition in Fe^{57}, another of the transitions following the Co^{57} decay. The 122-keV γ-ray energy is given by Greenwood,

TABLE I. Outer-shell conversion ratios for the 14.4-keV transition in Fe^{57}.

Source preparation	$M_{2,3}/M_1$	N_1/M_1
500-eV Co^{57} ions on graphite, “metallic” state	0.077 ± 0.007	0.034 ± 0.003
“0”-eV Co^{57} ions on graphite, “oxide” state	0.079 ± 0.007	0.024 ± 0.002
Theory [a] (pure *M*1)	0.080	

[a] See Ref. 10.

Helmer, and Gehrke[12] as 122.060 ± 0.010 keV. The K binding energy to the Fermi level for the neutral atom is given in Bearden and Burr[13] as 7112 ± 0.9 eV and in Ref. 7 as 7114 eV with uncertainty of ~1 eV. We take the later photoelectron[7] value, 7114 eV, and assume an uncertainty of ±2 eV. In addition the spectrometer work function (aluminum) is taken as 4 ± 1 eV, and for the "oxide" source, the chemical shift is 3.3 ± 0.4 eV. For the oxide source this results in a K_{122} energy of 114.939 ± 0.010 keV, the quoted γ-ray error dominating all others.

Table IV gives energies in the vacuum of the aluminum β spectrometer of the M_1 and N_1 conversion electrons from the two sources. Since the energy of the 14.4-keV transition is known to a fraction of an eV, namely, 14 412.5 ± 0.2 eV from the work of Bearden,[14] the binding energies of the M_1 and N_1 shells can be calculated by subtracting the line energies and the spectrometer work function from the γ-ray energy. These results are listed along with the binding energies given in two well-known experimental compilations. Our results are closer to the electron spectroscopy for chemical analysis (ESCA)[7] table than to the Bearden and Burr[13] values for the M_1 binding energy. While we have labeled the highest-energy conversion line from the 14.4-keV transition as "N_1", it is not clear that these valence electrons in the unspecified solid substrate should be labeled with specific shell nomenclature. Operationally, our result is that there is in both solid samples a group of electrons bound below the Fermi level of the solid by 7 or 8 V. In comparison, the first ionization potential in free neutral-atom Fe is 7.9 eV.

A large part of the error in the line energies originates in the calibration line uncertainty, which to some extent is suppressed in looking at line shifts only. Thus, for the two chemical states shown here, the K line shift is 3.3 ± 0.4 eV, the M_1 shift is 1.2 ± 0.9 eV and the N_1 shift is 1.2 ± 1.0 eV; in all cases the oxide state exhibits the larger binding energy.

Turning finally to the relative shapes of the N_1 and M_1 lines as shown in Figs. 2 and 3, we remark again that differences in line shapes on the same sample for lines which are only 100 eV apart at 14 keV are not expected to result from the energy dependence of inelastic losses occurring outside the original atom. Reasons for the larger width and considerable excess of tail area in the M_1 line shape must be found in some process in the original atom. One such process known to occur is the simultaneous ejection of another orbital electron with a conversion electron due to the sudden change in the atomic Coulomb field during the conversion event. This process, known as "shakeoff," has been observed accompanying photoelectric events,[15] K internal conversion,[16] and the various types of β decay.[17] In shakeoff with conversion the available energy (the conversion line energy minus the binding energy of the shakeoff electron in the ion) is shared continuously by the electrons, but most of the energy is usually taken by one, the "complementary" partner. (The shakeoff electron spectrum itself has its maximum intensity near zero energy.) The upper end point of this complementary spectrum lies on the tail on the conversion line. Shakeoff probability depends on the square of the effective change in charge[18] seen by any shell. For a vacancy created in a given shell, this effective change will be much smaller in that shell and inner shells than it is in shells exterior to the vacancy, and the shakeoff probabilities may thus be an order of magnitude smaller in the same and in inner shells than in exterior shells. Thus, if shakeoff of $M_{4,5}$ or N_1 electrons were responsible for some of the low-energy tail of the M_1 line, it would be expected that the N_1 line would have much less of that component, since the electrons ($3d$ and $4s$) effectively in the same shell as the conversion electron cannot readily be shaken off.

TABLE II. Relative [to L_1 at 10 (arbitrary) units] conversion line intensities of the 14.4-keV transition in Fe^{57}.

	K	L_1	L_2+L_3	$M+N$
Ref. 11	107 ± 25	10	0.92 ± 0.07	1.75 ± 0.2
Present work	114 ± 10	10	0.93 ± 0.07	1.69 ± 0.09
Theory[a] (pure $M1$)	106.6	10	0.850	1.58 (M only)

[a] See Ref. 10

In order to explore such an idea more quantitatively, the N_1 line shape is subtracted from the M_1 line shape (with peak normalization and matched on the high-energy side; insert of Figs. 2 and 3) and the area of the difference compared with the M_1-line area. The result is that the line-shape difference is:

(a) "zero"-eV ions (oxide) source, (32 ± 7)% of the

TABLE III. Ratio of total to K conversion (α_T/α_K) of the 14.4-keV transition in Fe^{57}.

	$10^3[(\alpha_T/\alpha_K)-1]$
Ref. 11	118 ± 25
Hall and Albridge[a]	121 ± 6
Present work	111 ± 10
Theory (pure $M1$) (Ref. 10)	116

[a] D. C. Hall and R. G. Albridge, Nucl. Phys. A91, 495 (1967).

M_1 area; and
(b) "500-eV" ions (metallic) source, (26 ± 5)% of the M_1 area.

According to Carlson *et al.*[18] for β^- decay (nuclear change in charge of 1 unit) the probability for shakeoff is the following: N_1 – 15.1% and $M_{4,5}$ – 9.6% for a total of 25%. These numbers must be reduced because the change in charge for the shells in question during M_1 conversion is less marked than during β^- decay. The usual screening rules[19] indicate that the $M_{4,5}$ contribution would be about the same, at 9.6%, and the $N_1 \approx (0.85)^2 \times 15\% \approx 11\%$ for a total of 20%. This is lower than the experimental numbers but the uncertainty in both still admits the hypothesis that shakeoff accounts for a substantial part of the M_1 tail excess.

Another test would be the shape of the shakeoff spectrum. This again is just the difference in the M_1 and N_1 shapes. These subtractions are shown in Figs. 2 and 3. The shapes should look approximately the same if this is a shakeoff effect. Although the errors are large (arising in the uncertainties of the N_1 tail), there is a rough similarity in the abrupt rise (essentially instrumental) to that characteristic of shakeoff complementary continua[15,16] and of the discrete transitions to unoccupied bound states ("shakeup").[20] We cannot say much about the character of the drop-off of the continua, because the N_1 tails cannot be extended much farther with these data. The energy displacement down from the M_1 line is estimated to be between 10 and 20 eV from the experimental data, i.e., from the position of the M_1-N_1 difference rise with respect to the M_1 line, allowing for the instrumental resolution. This range includes twice the valence-shell binding energy for the neutral atom; Krause, Carlson, and Dismukes[15] found for the displacement about twice the neutral-atom binding energy in the case of valence-shell shakeoff accompanying K-shell photoionization in gaseous argon and neon.

Another original-atom effect to be considered is the energy splitting of the 3*s* level as observed in Mn and Fe by Fadley *et al.*,[21] which they describe as the different exchange-interaction effects[22] on spin-up and spin-down core electrons in systems with unpaired outer-shell electrons.[23] This splitting will consequently vary with chemical state. Their experimental results show two lines near the expected 3*s* photoelectron energy when samples of Mn and Fe in various chemical states are irradiated with Mg Kα radiation. The lower-energy component in Fe (metal) is about 28% and for FeF_3 is about 40% of the total 3*s* intensity. The separation of the two components is 3.5 to 4 eV. Thus, while the intensity of the lower-energy component is approximately what we see in our M_1-N_1 line-shape difference, the energy displacement from the M_1 line in our work is much larger.

In summary, the difference between the M_1 and N_1 shapes is more probably due to shakeoff than to 3*s* exchange splitting. Our linewidth of 21 eV (N_1 line) is large compared to the splitting seen by Fadley *et al.*,[21] so that our 3*s* lines are not inconsistent with the splitting observed by them. On the other hand their results show no evidence for a shakeoff continuum beginning 10 to 20 eV below the 3*s* lines. Their available kinetic energy of ~1150 eV is >50 times the binding energy of the $M_{4,5}$- and N_1-shell electrons which, according to experiments of Carlson, Moddeman, and Krause[24] is more than enough to warrant expectation of full "sudden approximation" shakeoff intensities. If,

TABLE IV. Energies of the M_1 and N_1 conversion lines of the 14.4-keV transition in Fe^{57} and the binding energies to the Fermi level of the solid for the M_1 and N_1 shells. Energies are in electron volts (eV).

Source	M_1 Line energy	M_1 Binding energy	N_1 Line energy	N_1 Binding energy
This expt. ("metallic" state)	14 313.4 ± 2	95.1 ± 2	14 401.7 ± 2	6.8 ± 2
This expt. ("oxide" state)	14 312.2 ± 2	96.3 ± 2	14 400.5 ± 2	8.0 ± 2
Ref. 13		92.9 ± 0.9		3.6 ± 0.9 [a]
ESCA [b]		95		6 [a]
Lotz [c] (free atom)		98		7.87
First ionization (Ref. 9) potential of neutral free atom				7.90 ± 0.01

[a] Listed as $M_{4,5}$.

[b] Appendix I of Ref. 7. Error stated to be order of 1 eV.

[c] W. Lotz, J. Opt. Soc. Am. 58, 915 (1970).

however, one considers that their linewidth is only 3.5 eV and that the complementary spectrum might take ~10 eV to get down to half the initial-step intensity (see Ref. 15, Fig. 5), then for a shakeoff spectrum with 20% of the line area the initial step might be only ~7% of the peak height. So small a feature could not be ruled out in the data of Fadley *et al.*[21] (see their Fig. 1). Thus, the interpretation of the difference in our M_1 and N_1 line shape as resulting from more shakeoff for the M_1 line is not inconsistent with their data.

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