

Study on X-ray and electron-excited fluorescence spectroscopy of tungsten using TES

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Abstract

In the exploration of celestial bodies, such as Mars, the Moon, and asteroids, X-ray fluorescence analysis has emerged as a critical tool for elemental analysis. However, the varying selection rules and excitation sources introduce complexity. Specifically, these discrepancies can cause variations in the intensities of the characteristic spectral lines emitted by identical elements. These variations, compounded by the minimal energy spacing between these spectral lines, pose substantial challenges for conventional silicon drift detectors (SDD), hindering their ability to accurately differentiate these lines and provide detailed insights into the material structure. To overcome this challenge, a cryogenic X-ray spectrometer based on transition-edge sensor (TES) detector arrays is required to achieve precise measurements. This study measured and analyzed the K-edge characteristic lines of copper and the diverse L-edge characteristic lines of tungsten using a comparative analysis of the electron and X-ray excitation processes. For the electron excitation experiments, copper and tungsten targets were employed as X-ray sources, as they emit distinctive X-ray spectra upon electron-beam bombardment. In the photon excitation experiments, a molybdenum target was used to produce a continuous spectrum with the prominent Mo $K\alpha$ lines to emit pure copper and tungsten samples. TES detectors were used for the comparative spectroscopic analysis. The initial comparison revealed no substantial differences in the K α and K β lines of copper across different excitation sources. Similarly, the L α lines of tungsten exhibited uniformity under different excitation sources. However, this investigation revealed pronounced differences within the $L\beta$ line series. The study found that XRF spectra preferentially excite outer-shell electrons, in contrast to intrinsic spectra, owing to different photon and electron interaction mechanisms. Photon interactions are selection-ruledependent and involve a single electron, whereas electron interactions can involve multiple electrons without such limitations. This leads to varied excitation transitions, as evidenced in the observed $L\beta$ line series.

Keywords X-ray spectra \cdot X-ray emission spectra and fluorescence \cdot Superconducting transition-edge sensor \cdot X-ray and γ -ray spectrometers

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1 Introduction

X-ray fluorescence analysis has played a significant role in material elemental identification and charge state measurements during exploration of Mars, the Moon, and asteroids [1–3]. It also has important applications in advanced light sources [4–8] and scanning electron microscopy [9–11]. Depending on the practical scientific application, various excitation sources can be used, including X-ray sources [1, 12], electron excitation sources [13–15], proton excitation sources [16–18], and α particle excitation sources [2, 19, 20]. X-ray sources mainly include X-ray tubes, synchrotron radiation sources, and free-electron lasers, and they have

the widest range of applications. Electron excitation sources include β -ray sources and electron guns, with electron guns being primarily used in electron-beam etching, scanning electron microscopy, and transmission electron microscopy. Proton sources are primarily small accelerators, whereas α particle excitation sources include radioactive sources and accelerators. Other excitation sources such as heavy ion and neutron sources are relatively complex and will not be discussed here.

The interaction mechanisms between the various excitation sources and materials are significantly different [17. 21-24]. The interactions of photons and electrons with atoms, for instance, exhibit distinct differences with regard to selection rules and energy-momentum conservation restrictions, etc. This results in varying processes and probabilities of the excitations for electrons located in different atomic shells when interacting with photons and electrons [24–26]. First, owing to the constraints of energy and momentum conservation, when the energy of a photon is absorbed by an outer-shell electron, triggering its ejection, the required momentum is supplied by the atomic nucleus. Therefore, the stronger the interaction between the electron and the atomic nucleus, the more easily the electron is excited. Hence, photons exhibit a higher propensity to excite inner-shell electrons during interactions with atoms. Second, because photons are electrically neutral, they mainly interact with one electron upon incidence. When a photon interacts with an outer-shell electron and is absorbed, the corresponding electron can only transition to certain energy levels and spin states. This indicates that specific selection rules must be complied with during this process.

In contrast, electrons, unlike photons, do not vanish after interacting with the outer-shell electrons and do not require momentum from the atomic nucleus. Additionally, the stronger the bond between the atomic nucleus and the outershell electrons, the more difficult it is for incident electrons to excite them. This is why electrons tend to excite outershell electrons more readily when they interact with atoms. Furthermore, when charged, electrons interact with multiple outer-shell electrons upon incidence. Finally, because electrons do not disappear before or after interactions with atoms, and can simultaneously interact with multiple outershell electrons, the excitation process does not need to conform to specific selection rules. Owing to the disparities in the electron shells and spin states excited by electrons and photons, differences may arise in the transition paths, as well as in the intensity of these transitions, reflecting the differing probabilities of each type of excitation event. Such differences among the excited electrons could lead to variations in the intensities of the characteristic spectral lines emitted by the same element during de-excitation. These variations in transition probabilities and their resultant spectral lines, in terms of both relative intensities and likelihood of



Fig. 1 (Color online) A schematic diagram illustrating the energylevel transition paths corresponding to the electron shells and various fluorescence spectral lines in an atom. The electron shells outside the atomic nucleus include *K*, *L*, *M*, *N*, etc., with the number of subdivided energy levels being 1, 3, 5, and 7, respectively, as indicated in the corresponding levels in the lower-right corner of each electron shell. The energy-level transition path corresponding to each fluorescence spectral line is provided in parentheses, representing the transitions of electrons from outer shells to vacancies in inner shells, with the emission of fluorescence spectral lines corresponding to the initial and final levels. The α -line and partial β -line and γ -line series are depicted as the primary spectral lines in the schematic; the other spectral lines are not shown

occurrence, are critical for interpreting spectral data. The energy-level transition paths pertaining to the electron shells and fluorescence spectral lines are depicted in Fig. 1.

The differences in the excitation processes between electrons and photons primarily affect the outer-shell electrons, which exhibit a more significant impact than the inner-shell electrons. This is because the outer-shell electrons are more susceptible to variations in excitation energy and interaction mechanisms. As a result, discrepancies in the spectral lines, particularly in the are more pronounced because these series involve transitions that are significantly influenced by the state of the outer-shell electrons. On the other hand, the α -line series, which results from transitions between the K and L shells, is characterized by more stable interactions, and thus shows less variation. A challenge arises when comparing the spectral lines of the β -line and γ -line series, which exhibit small energy separations (typically less than 100 eV, and in some cases, as minimal as 10 eV) for practical scientific applications. Such narrow energy gaps make it difficult to measure materials and identify elements using conventional detection devices such as silicon drift detectors (SDD). The energy resolution of an SDD is approximately 120 eV, which is insufficient for discriminating the narrowly separated individual spectral lines. To obtain more precise and detailed information about material structures, it is crucial to utilize a detector capable of high-energy resolution across a wide energy range [27–30]. A detector using a superconducting transition-edge sensor (TES) can perfectly satisfy these requirements. By utilizing cryogenic X-ray spectrometers equipped with TES detectors, we can more effectively discern and accurately measure spectral features, particularly for the precise distinction of the spectral lines in the β -line and γ -line series, and relevant measurements can then be performed [31–36].

In this study, the TES detectors demonstrated superior energy resolution and detection efficiency for X-rays within the energy range of 1.5 keV to 17.0 keV [33, 37–39]. Therefore, certain spectral lines within this range were selected for analysis. The *K* characteristic lines of copper (Cu) lie between 8 keV and 9 keV, whereas the *L* line series of tungsten (W) also falls within the sensitive range of our spectrometer. Therefore, both copper and tungsten are ideal candidates for our comparative study of the spectral differences observed between electron and X-ray excitation.

Although an electron gun linked to a high-vacuum chamber is the optimal electron source for generating an electroninduced X-ray spectrum, implementing such an arrangement adds significant complexity to the experimental setup. To achieve a practical solution, we used commercially available X-ray tubes with copper and tungsten targets, which essentially replicate electron excitation by bombarding the anode material with high-energy electrons. These X-ray tubes provide a more accessible means of obtaining electron excitation spectra, theoretically akin to an electron gun setup. For the photon excitation spectra, we utilized the molybdenum (Mo) target X-ray tube generating X-ray radiation to irradiate high-purity copper and tungsten samples. By employing TES detectors to separately acquire and analyze the resultant energy spectra from the electron and photon excitations, we can discern and compare the K characteristic lines of copper and L characteristic lines of tungsten excited by either electrons or photons. The use of TES detectors was pivotal in this study, as they provided the acute energy resolution necessary to discern subtle differences and obtain definitive results.

2 Measurement and analysis

2.1 Experimental setup

Our chosen electron source for the experiment comprised X-ray tubes that utilize accelerated and focused electron beams to excite the metal samples and generate X-rays [25]. In the electron source, high-energy electron beams are injected into copper or tungsten targets. The principle underlying this X-ray generation is the interaction between the injected high-energy electron beam and the target atoms.

When electrons in the beam encounter the atoms in the metal, they can either ionize them through collisional ionization or excite atomic electrons to higher energy levels. These excited electrons undergo transitions and return to lower energy levels, and in the process, they emit characteristic X-ray spectral lines indicative of their elemental origins.

In addition, we utilized a molybdenum target X-ray tube as the photon source to interact with high-purity copper and tungsten samples. In the X-ray tube, molybdenum atoms emit X-ray photons when an electric current is applied. These emitted X-rays possess the energy necessary to excite the high-purity copper and tungsten samples, thus exciting their inner-shell electrons. As these excited electrons return to their ground state, the released energy is emitted in the form of X-ray photons. These photons carry quantized energies that are characteristic of the element involved, thereby generating X-ray fluorescence (XRF) spectra with distinct energies and frequencies.

Theoretically, the adjustable parameters of the X-ray tube, such as the current and voltage settings, heavily influence the spectral output by determining the intensity and energy distribution of the emitted X-rays. In electron excitation experiments, X-ray tube parameter adjustment is crucial for controlling the spectral output of the electron excitation of copper and tungsten targets. The acceleration voltage (V) is meticulously set above the threshold excitation voltage ($V_{\rm th}$) of the target material, which leads to the generation of a spectrum predominantly characterized by the inherent spectral lines of the material, supplemented by a continuous X-ray background, i.e., Bremsstrahlung. As V increases beyond $V_{\rm th}$, an increase in the intensity of the characteristic lines ($I_{\rm ch}$) can be observed according to the empirical relationship.

$$I_{\rm ch} \propto k_{\rm ch} (V - V_{\rm th})^m \tag{1}$$

Following this, Fig. 2 presents the schematics of the source, interaction, and detector, illustrating the entire X-ray generation and detection process. Additionally, TES detectors were introduced to detect and analyze the emitted X-rays, which allowed for the high-resolution observation and precise interpretation of the excited X-ray energies [34].

2.2 Measurement and results

To obtain the intrinsic spectra of copper and tungsten using the electron source, it is essential to appropriately adjust the experimental conditions. For copper, with its *K*-edge at 8.980 keV, we selected voltage settings of 11 kV, 12 kV, 13 kV, and 14 kV to ensure that the beam's energy surpassed this threshold, facilitating the excitation of the characteristic lines of copper. Similarly, because the L_1 , L_2 , and L_3 edges of tungsten are 12.102 keV, 11.540 keV, and 10.200 keV, the voltage settings of the tungsten target were 15 kV, 16 kV, 18 kV, and 20 kV, respectively. For both targets, the currents were carefully selected from the milliampere (mA) range to achieve the required energy levels. The electron beam was accelerated and focused to generate the desired energy levels necessary for these experiments, with each run lasting approximately 12 h to ensure sufficient data of adequate quality and statistical significance.

Regarding the use of the X-ray source, for the molybdenum target with the K-edge of molybdenum at 20.000 keV, the most intense $K\alpha_1$ line energy produced was 17.479 keV, which provided sufficient energy to excite the inner-shell electrons in the studied samples. Consequently, the voltage settings for the molybdenum target to illuminate the pure metal were chosen as 30 kV, 40 kV, 45 kV, and 50 kV. The corresponding current levels were chosen in the appropriate ampere (A) range to effectively optimize the sample excitation and X-ray emission within the desired energy range. Subsequently, the XRF mode was employed to obtain the energy spectrum. Given the negligible differences in spectra across various experimental setups, except for count rate variations, the results at the 50 kV setting were adopted as a benchmark for further analyses, ensuring a standard reference point for comparing X-ray emission efficiencies and sample excitations across the experiments.

Figure 3 illustrates a comparison of the intrinsic spectrum of copper acquired from the electron source and the corresponding XRF energy spectrum derived from the photon source. For the electron-source-derived spectra, we applied voltages ranging from 11 kV to 14 kV to the copper target for a comprehensive analysis. In contrast, for the photon source, the spectrum resulting from the 50 kV configuration using a molybdenum target is presented because it consistently provided representative data. All data were processed after calibration and normalization procedures before analysis, and compared with the spectrum obtained under similar experimental conditions using the SDD detector. Our analysis shows that for the copper *K*-edge energy range, the characteristic $K\alpha$ and $K\beta$ lines exhibited remarkable consistency across the two different excitation sources.

The normalization approach applied in Fig. 3 for copper leverages the $K\alpha$ peaks, comprising $K\alpha_1$, and $K\alpha_2$. These peaks correlate with the energy-level transitions of KL_3 and KL_2 in copper, respectively. From our analysis, it is notable that across varying voltages within the intrinsic and XRF energy spectra, the intensities of the left $K\beta$ lines exhibited no significant variations under either the electron or photon excitation sources. This result aligns with the theoretical understanding that the transition paths of all *K* line series are associated with the *K* shell, which is a singular energy level without subshell divisions. Upon further scrutiny of the spectral behavior, we confirmed that the total counts and spectral line probability densities for the copper *K* line series were substantial, which guaranteed the detection result.

Similarly, Fig. 4 compares the intrinsic spectrum of tungsten elicited by the electron source and the XRF energy spectrum of tungsten obtained using the photon source. The operational voltages of the tungsten target for the electron source were 15 kV, 16 kV, 18 kV, and 20 kV. For the photon source analysis, a 50 kV configuration using a molybdenum target was selected as a representative example. All data were processed after calibration and normalization procedures and compared with the spectrum obtained under similar conditions using the SDD detector. A comparative analysis revealed that within the energy range of the characteristic lines of the *L*-edge of tungsten, the *L* α lines



Fig. 2 (Color online) **a** The X-ray generation process involves the utilization of accelerated and focused electron beams as the electron source to excite metal samples. **b** The generated X-ray photon acts as

the incident X-ray source to stimulate X-ray generation in a metallic target for fluorescence spectroscopy. c The superconducting TES is utilized for high-resolution X-ray detection



Fig. 3 (Color online) A comparison of the intrinsic and XRF energy spectra of copper obtained from electron and photon sources, respectively. The copper target was operated at voltages of 11 kV, 12 kV, 13 kV, and 14 kV for the electron source, and a 50 kV configuration using a molybdenum target was used as a representative example for the photon source. The data underwent calibration and normalization, and were compared with the spectrum obtained under similar conditions using the SDD detector (light blue). Similarity was observed in the $K\alpha$ and $K\beta$ lines within the *K*-edge energy range across different excitation sources

of tungsten showed no noticeable variations under different excitation sources. However, distinct differences were observed within the $L\beta$ line series. For a focused examination of these discrepancies, the energy spectra within the $L\beta$ line energy range were enlarged and compared, selecting the intrinsic electron source spectrum at representative voltages of 15 kV and 20 kV, along with the XRF energy spectrum of tungsten obtained from the photon source, as shown in Fig. 5a. In particular, for the intrinsic electron source spectrum at a representative voltage of 20 kV, each peak within the $L\beta$ line energy range was analyzed and marked with its energy-level transition path. To complement this, Fig. 5b provides a schematic of the energy-level transition paths for the corresponding illustration.

The normalization process shown in Fig. 4 was performed based on the peak intensities of the $L\alpha$ lines of tungsten, including $L\alpha_1$ and $L\alpha_2$, corresponding to the energy-level transition paths of L_3M_5 and L_3M_4 , respectively. Additionally, the enlarged Fig. 5a shows that the peak intensities of $L\beta_2$ (L_3N_5) and $L\beta_6$ (L_3N_1) were consistent with the $L\alpha$ lines across various representative voltages within the intrinsic and XRF energy spectra. This observation suggests that the spectral lines resulting from the de-excitation process of excited electrons related to the same outermost energy level, the L_3 subshell, exhibit similar peak intensities. For the other characteristic spectral lines, the peak intensities of $L\beta_4$ (L_1M_2) and $L\beta_3$ (L_1M_3), associated with the innermost energy level of the *L*-edge, the L_1 subshell, were noticeably



Fig. 4 (Color online) A comparison between the electron-induced intrinsic and photon-induced XRF energy spectra of tungsten. For the electron source, voltages of 15 kV, 16 kV, 18 kV, and 20 kV were employed, while the photon source utilized a 50 kV molybdenum target setting. The data underwent calibration and normalization, and were compared with the spectrum obtained under similar conditions using the SDD detector (light blue). No significant variations were observed in the $L\alpha$ lines series, but distinct differences were observed within the $L\beta$ line series within the *L*-edge energy range under different ent excitation sources

weaker in the intrinsic energy spectrum than in the XRF energy spectrum. This reflects the lower probability of exciting electrons in the inner subshell compared to the outer subshell during electron excitation. Similarly, the peak intensity of $L\beta_1$ (L_2M_4), related to the subouter energy level, the L_2 subshell, was weaker in the intrinsic spectrum than in the XRF spectrum. Moreover, we detected a unique peak located at the high-energy end near $L\beta_1$ in the intrinsic energy spectrum, which was absent in the XRF spectrum. Accurately targeting the energy value of this peak center allows it to be numerically matched with the energy difference between the L_2 and M_5 levels. However, L_2M_5 is an energy level that contravenes the selection rules; thus, it is not represented as a characteristic energy level in the XRF energy spectrum. This finding indirectly verifies the initial assertion that specific selection rules are obligatory in the photon excitation process, whereas electron excitation is not bound by these rules.

Drawing on the foundational concepts introduced in the Introduction and reinforced by our experimental data, we can establish that photons and electrons engage with atomic structures under profoundly different constraints of energymomentum conservation and selection rules, dictating the likelihood and nature of electron excitation across various atomic shells. Building upon the meticulous analytical observations delineated for both copper in Fig. 3 and tungsten in Fig. 4, our discussion further elucidates the intricate dynamics of electron excitation and photon interaction within these





Fig. 5 (Color online) **a** An enlarged comparison of energy spectra within the $L\beta$ line energy range for the intrinsic spectrum of tungsten (at representative voltages of 15 kV and 20 kV) from the electron source and XRF energy spectrum of tungsten from the photon source. Each peak of the intrinsic electron source spectrum at a volt-

elements, as evidenced by their spectral behaviors. For copper, the consistent behavior of the K line series underlines the singular nature of the K shell, which is a foundational aspect that underpins our understanding of the electron structure and transition probabilities within this metal. The uniform response across varying excitation modes not only underscores the theoretical frameworks guiding our interpretations but also highlights the robustness of the detection methodologies employed, ensuring the reliability of the observed spectral features. As for tungsten, the contrast in the peak intensities between the $L\alpha$ and $L\beta$ lines clarifies the nuanced differences attributed to the subshell configurations within the *L*-edge. The variations observed in the $L\beta$ line series capture the inherent variations in the excitation probabilities between the inner and outer shells during electron interactions. This asymmetry underscores the role of charged electrons in readily exciting outer-shell electrons, as opposed to their neutral photon counterparts, which abide by selection rules and are more likely to interact with inner-shell electrons. Especially noteworthy is the revelation provided by the unique peak near the $L\beta_1$ line, an anomaly that poses a challenge to conventional selection rules and paves the way for a deeper investigation into the mechanics of electron excitation versus photon excitation. This anomaly enriches our understanding of tungsten's spectral lines under diverse excitation scenarios, highlighting an excitation pathway that is available only to electron excitation.

age of 20 kV within the $L\beta$ line energy ranges is marked with the corresponding energy-level transition path. **b** A schematic diagram illustrating the energy-level transition paths corresponding to the electron shells and various fluorescence spectral lines of $L\alpha$ and $L\beta$ series mentioned in (a)

3 Conclusion and outlook

In conclusion, our study provides insight into the spectral responses of copper and tungsten when subjected to various excitation sources. For copper, the experimental data revealed that the intensities of the $K\alpha$ and $K\beta$ lines remained constant across the electron and photon excitation methods. This observation aligns with theoretical insights into the structure of the K shell, suggesting that the lack of subshell divisions results in uniform transitions that are less sensitive to the type of excitation source used. In contrast, the spectral analysis of tungsten demonstrated distinct behaviors, especially for $L\beta$ lines under varying excitation sources. Although the $L\alpha$ lines were consistent, the $L\beta$ lines displayed notable variations, which can be attributed to the complex subshell configuration and its influence on the excitation and de-excitation processes.

Looking ahead, the findings of our current study can serve as a springboard for advancing our understanding of atomic excitation dynamics and spectroscopic analysis. With the nuances of spectral line behaviors now in sharper focus, our upcoming research initiatives will aim to refine the methods we use to analyze and interpret data from an expanded spectrum of materials. An electron gun spanning a 1 keV to 30 keV energy range has been procured for the laboratory, and the development of a matching high-vacuum chamber is already in progress. These tools will allow us to extend our investigations to metals beyond copper and tungsten and delve into the intricacies of the $L\beta$ line series across different elements. A TES detector equipped with a sufficiently high-energy resolution and wide-range capability promises a more meticulous deconstruction of individual spectral lines. This development is intended to reveal finer details of material structures, offering a richer dataset for energy-dispersive spectroscopy applications, particularly within the realm of electron microscopy.

Furthermore, experiments are planned using Am-241 as an α particle source to juxtapose and contrast the energy spectra evoked by electron versus α particle interactions. These research endeavors will ultimately establish a comprehensive database. This reservoir of knowledge is envisioned to function in sync with sophisticated space science instruments such as APXS, enhancing both terrestrial and extraterrestrial material analyses. Through these ambitious projects, we aim not only to bolster the foundation of spectroscopy, but also to contribute a significant corpus of data and analytical expertize to the expansive fields of material science, chemistry, and astrophysics.

Author Contributions Shuo Zhang contributed to the study conception and design. Material preparation, data collection, and analysis were performed by Bing-Jun Wu, Jing-Kai Xia, Wen-Tao Wu, and Robin Cantor. The first draft of the manuscript was written by Bing-Jun Wu and Jing-Kai Xia, Jin-Hua Li, Xiao-Ming Xie and Zhi Liu do the supervision, and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

Data Availability The data that support the findings of this study are openly available in Science Data Bank at https://cstr.cn/31253.11.scien cedb.j00186.00365 and https://doi.org/10.57760/sciencedb.j00186.00365.

Declarations

Conflict of interest Zhi Liu is an editorial board member for Nuclear Science and Techniques and was not involved in the editorial review, or the decision to publish this article. All authors declare that there are no conflict of interest.

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