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HEAVY-ION-INDUCED X-RAY SATELLITE EMISSION AS A CHEMICAL PROBE

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ABSTRACT

Advances in energy technology often require corresponding advances in materials fabrication and characterization. Among the new techniques being developed for the improved characterization of materials is an x-ray fluorescence method which uses heavy ions for excitation. High resolution measurements of heavy-ion excited x-ray spectra have revealed a series of prominent satellite lines in addition to the normal emission lines. It has been shown that these satellites display intensity variations indicative of the chemical state or environment of the emitting target atom and the projectile velocity. In order to evaluate heavy-ion induced x-ray satellite emission (HIXSE) as a chemical probe, we have examined a series of sulfur compounds and titanium, vanadium and molybdenum alloys and compounds. Results will be presented which demonstrate the chemical sensitivity of this technique, the range of elements which can be analyzed and the potential for applications to real chemical and materials problems.

INTRODUCTION

New materials with improved physical properties such as strength and ductility are being developed for use in the field of energy technology. Future advances in this field may depend upon the characterization of not only the elemental composition of these materials but also the chemical nature or bonding of their constituents. Among the new techniques being developed for the chemical characterization of materials is an x-ray fluorescence method which uses fast, heavy-ions for excitation. In this paper, the analytical potential of heavy-ion induced x-ray satellite emission (HIXSE) as a probe of the chemical environment of an element in a solid will be examined in terms of its chemical sensitivity, the range of elements which can be analyzed and by the application of the technique to chemical and materials problems. Future trends for HIXSE will also be discussed.

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Chemical Sensitivity

The relaxation of an atom with a core level vacancy can occur through the emission of an x-ray. Without any knowledge of how the vacancy was produced, the identity of the emitting atom can be determined by the characteristic energy of the radiation. For example, an emission line at 4.93 keV corresponds to the $K\beta$ ($1s \rightarrow 3p$) transition of titanium. The intensity of the line, however, depends in part upon the efficiency or cross section for producing a K-vacancy in the titanium target. While different excitation sources such as electrons, photons, and charged particles have different x-ray production efficiences, each has unique analytical advantages. Fast (10^9 cm/sec) heavy-ions, for example, have a high cross section for producing multiple inner and outer shell vacancies. This results in a dramatic increase in the relative intensity of the satellite lines associated with the normal diagram line. Fig. 1 shows the high resolution titanium $K\beta$ satellite spectrum produced by the bombardment of titanium metal with 36 MeV Cl ions extracted from the Oak Ridge (model EN) tandem Van de Graaff. The peaks in this spectrum correspond to the Ti $K\beta$ x-rays emitted from configurations having n L-shell vacancies. As shown in Fig. 2, the analytical advantage of multiple vacancy production is that the intensity distribution of the satellite lines is sensitive to the chemical environment of the emitting atom. The Ti $K\beta L^n$ satellite spectra of Ti metal and TiO_2 have been corrected for mass absorption effects, projectile energy loss, and concentration effects.

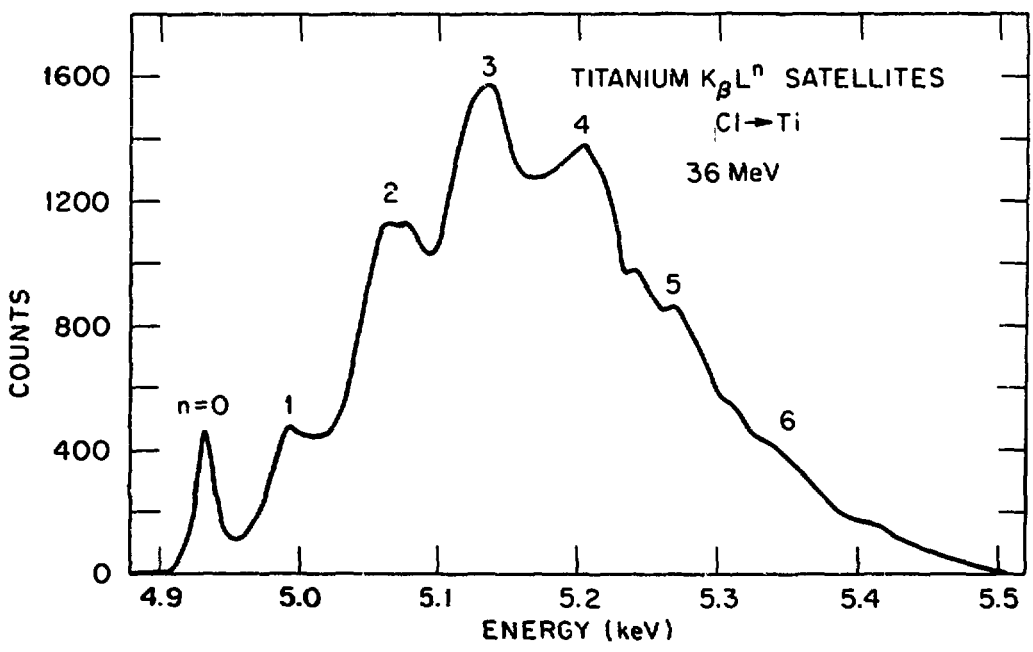

Fig. 1. The corrected titanium $K\beta L^n$ satellite spectrum produced by the collision of 36 MeV Cl ions with titanium metal.

The observed spectral variations between Ti metal and TiO_2 are the consequence of differences in the refilling rates of the L vacancies prior to the emission of the Kβ x-ray. Because the outer shell electrons are also removed during the collision process, the refilling of the L shell is believed to proceed through direct inter-atomic Auger transitions or by inter-atomic electron transfer to the valence level of the ion followed by rapid intra-atomic Auger cascading (ref.1,2). A change in the chemical environment or valence electron distribution will alter the electron transfer rates and thus change the observed satellite x-ray yield.

Initial attempts to correlate the $K\alpha L^n$ satellite intensity distribution of third row elements with the chemical environment used a parameter called the average L-vacancy fraction P_L (ref.2). It is defined as the apparent number of L-vacancies as determined by the weighted sum of the relative satellite intensities divided by the total number of possible vacancies. This parameter was shown to be linearly related to the bulk valence electron density (the number of valence electrons/$Å^3$) of the target material. We have recently shown in a study of the chemical effects on the $K\alpha L^n$ satellites of a series of sulfur compounds that individual satellite lines are more strongly influenced by the chemical environment than the aggregate satellite intensity distribution (ref.3).

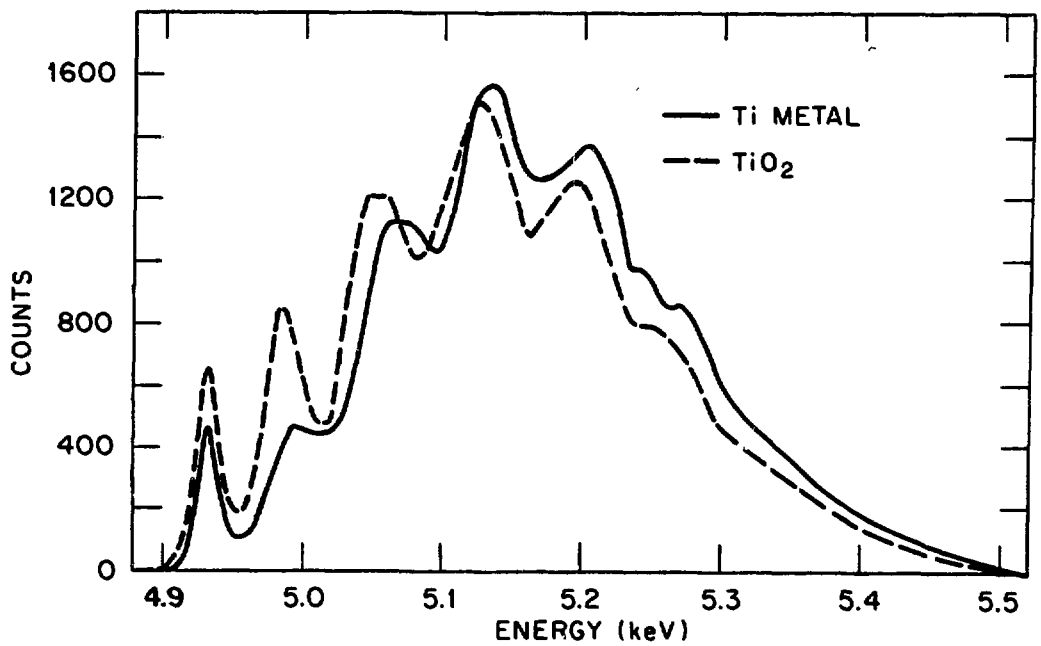

Fig. 2. The corrected titanium $K\beta L^n$ satellite spectra produced by the collision of 36 MeV Cl ions with titanium metal (solid line) and TiO_2 (dashed line).

Range of Elements

The utility of HIXSE as a chemical probe depends in part upon the range or variety of elements for which this technique is sensitive. Although it has been conclusively shown that the K_α transition is sensitive to the chemical environment of the second and third row elements, few studies have explored other regions of the periodic table (ref.4). Because the sensitivity of the K_α transition decreases as the number of shells between the L-shell and valence shell increases, the expansion of this technique to the transition metals, for example, is contingent upon the evaluation of the chemical shifts associated with other transitions. We have begun the necessary evaluation by exploring the $L_{\alpha,\beta}$ transition of molybdenum (ref.5) and the K_β transition of titanium and vanadium.

The corrected molybdenum L x-ray spectra produced by the collision of 1 MeV/amu Cl ions with various molybdenum bearing targets displayed variations in the intensity distribution of the L_α and L_β satellites (L^nM^m). Amplification of those variations was obtained by calculating difference spectra using the molybdenum metal spectrum as the subtrahend. It was found that a specific region of the difference spectra displayed a systematic correlation with the bulk valence electron density as shown in Fig. 3. It can be seen that

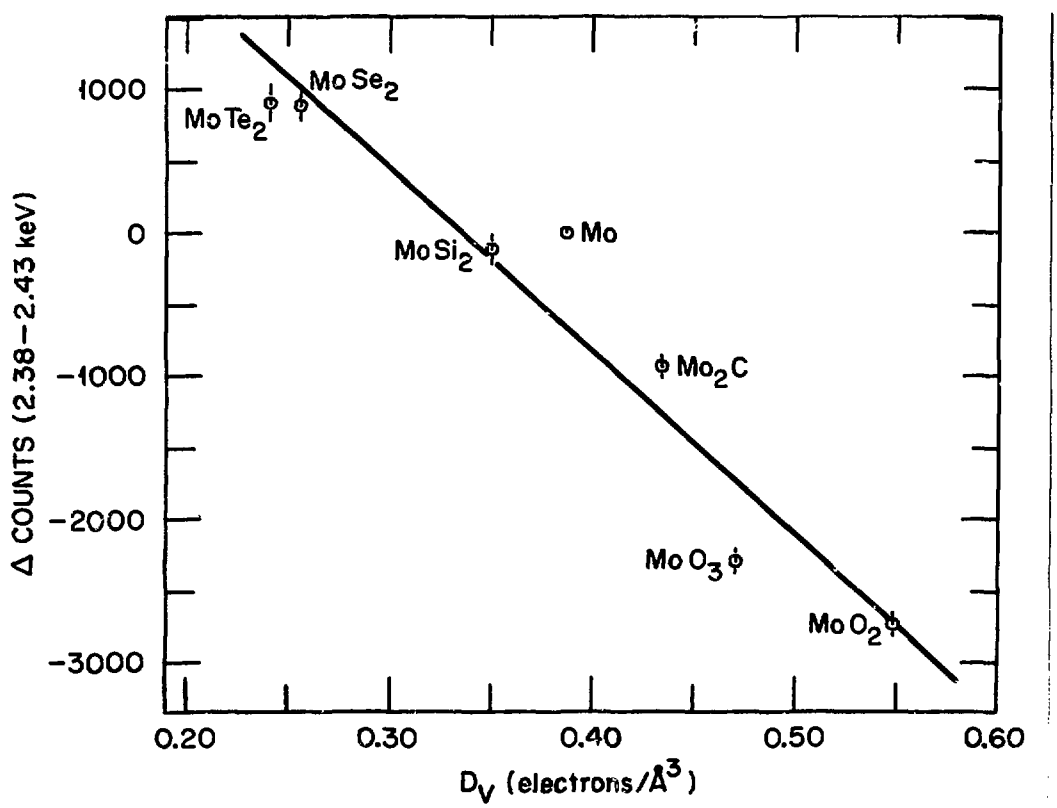

Fig. 3. The integrated difference counts in the 2.38-2.43 keV region vs the valence electron density of molybdenum compounds.

as the bulk valence electron density increases, the x-ray yield, relative to molybdenum metal, decreases. This indicates that the refilling mechanism, in agreement with the Kα results for second and third row elements (ref.2), occurs through inter-atomic electron transfer. Clearly the L x-rays can be used to probe the chemical state or environment of intermediate Z elements.

The **heavy-ion excited Kβ spectra** of a series of titanium and vanadium targets like the titanium spectra shown in Fig. 2, exhibited variations in their satellite intensity distribution for different chemical states. Systematic correlations await improved counting statistics.

Applications

The application of HIXSE to the characterization of the chemical environment of the constituents of alloys is another component of its development as an analytical probe. We have explored this avenue by examining a series of binary molybdenum alloys and a complex group of vanadium alloys (ref.6). In addition to observing variations in the L x-ray satellite spectra of molybdenum compounds, variations were also detected in the spectra of a series of molybdenum-titanium bcc alloys. We found, however, that a strong correlation with the bulk valence electron density exists only for a different region of the satellite difference spectra than that observed for compounds. The slope of the correlation was also reversed. These observations may be due to differences in the distribution of valence electrons between bonding partners. The valence electrons involved in metallic bonding, for instance, are more delocalized than those involved in ionic or covalent bonding. In addition, these systematic variations may be delineating metallic valence states. Just as a valence state can be used to describe inorganic compound formation, metal valence states may be useful for describing and predicting bonding and crystal formation of alloys. Further studies will explore this possibility.

A more severe test of the ability of HIXSE to probe the valence environment of alloys was the examination of the Kβ spectra of a group of long range ordered (LRO) alloys with the same composition ($V(Co_{.43}Ni_{.57})_3$) but different crystal structures. These materials are of interest because in the cubic form they possess unusual strength and ductility at high temperatures. Using the difference spectra approach described previously, we have shown that HIXSE can differentiate between an LRO alloy in an ordered cubic ($L1_2$) form and an ordered hexagonal ($BaPb_3$) form. Although it won't replace diffraction methods, the ability to detect changes in the valence electron distribution due to crystallographic alterations demonstrates the potential of HIXSE to probe metallic bonding in alloys.

Future Trends

The future of heavy-ion induced x-ray satellite emission (HIXSE) as a chemical probe will depend upon the expansion of the work described in this report. We will continue to use HIXSE to examine metallic bonding and metal valence states. Specifically, we will attempt to probe the valence states of a series of lanthanide metals by examining their L x-ray satellite spectra. The L x-ray spectra of zirconium alloys and compounds will also be evaluated. We expect these results to concur with the molybdenum results. In order to extend the range of elements which can be probed, we will appraise the chemical sensitivity of the M-transition for high Z elements (>68). New applications will also be evaluated. It was recently shown by Deconninck and Van den Broek (ref.7) that the heavy ion excited fluorine x-ray satellite spectra could be used to determine the formation of FeF_3 produced by F^- implantation of iron. This suggests that implanted ions could serve as a probe of the chemical environment of a host lattice. By judiciously choosing the probe ion, the sensitivity of HIXSE to the host could be maximized.

Finally, preliminary studies (ref. 8) have indicated that the chemical sensitivity of the Kα satellite spectra could be enhanced by increasing the resolution of the x-ray spectrometer. The satellite lines shown in Fig. 1 are actually composed of a large number of multiplet lines corresponding to the angular momentum coupling of the unpaired electrons. These individual transitions should be even more sensitive to changes in the refilling mechanism induced by the chemical environment than the peaks representing the overall vacancy configuration. A high resolution spectrometer is currently under development.

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