ADVANCES IN HIGH-RESOLUTION STUDIES OF THE CHEMICAL EFFECTS IN THE
MOLYBDENUM L HEAVY-ION-INDUCED X-RAY SATELLITE EMISSION (HIXSE) SPECTRA*

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ABSTRACT

High-resolution measurements of the molybdenum L heavy-ion-induced X-ray satellite emission (HIXSE) spectra of a series of Mo alloys and compounds have been obtained with a new, high-efficiency, high-resolution Bragg crystal spectrometer in the von Hamos geometry. The improved resolution (5 eV at 2.3 keV) is sufficient to reveal the L^{nM} configuration lines in the $L\alpha$ and $L\beta$ hypersatellite bands. Both sets of lines exhibit the same trend in the variation of the relative yield distribution with the chemical environment as was observed for KL^n lines of lower Z targets. Difference spectra, using elemental molybdenum as a subtractend, enhance the systematic variation. These results confirm the analysis and conclusions of lower resolution studies. They also indicate a potential for even greater sensitivity to the chemical environment.

INTRODUCTION

Heavy-ion-induced X-ray satellite emission (HIXSE) is a technique which uses fast, heavy-ions for excitation. The analytical utility of this method derives from its ability to probe the chemical environment of the emitting element. In order to develop an understanding of HIXSE, the well-known particle-induced X-ray emission (PIXE) technique will be described first. Modification of the PIXE experiment in two steps will illustrate the magnitude of and the explanation for HIXSE's chemical sensitivity.

In PIXE, a focused beam of energetic (1-3 MeV) protons or α particles impinges upon a target creating core level vacancies by coulombic excitation. The characteristic X-ray emission associated with the relaxation process and typically detected by an energy dispersive

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Fig. 1. The Ti $K\beta$ line from Ti metal excited by energetic protons (dot-dashed line) and Cl ions (dashed line) and the Ti $K\beta$ line of TiO_2 (solid line) excited by Cl ions.

Si(Li) detector, provides a means for determining the elemental composition of the sample. For example, bombardment of elemental titanium with a 3 MeV proton beam will result in the observation of resolved Ti $K\alpha$ and $K\beta$ lines. If the proton source is replaced with a heavy-ion source, e.g. a 36 MeV Cl ion beam, a change in the intensity of the K transitions is expected because of a change in the vacancy production cross section for heavy-ions.¹ Although a change in the relative intensity is observed, the approximately 200 eV shift in the energy of the peak, as shown for the Ti $K\beta$ transition in Figure 1, is more dramatic. Even more surprising is the almost 10 eV energy shift also shown in Figure 1 for TiO_2 . It is well known from X-ray absorption edge and ESCA measurements of metals and metal oxides that core levels shift approximately 1 to 4 eV in energy.² It is also known that, because the energy of the X-ray fluorescence is a measure of the difference between two core levels shifting nearly the same amount, the fluorescence chemical shift is usually less than 0.3 eV for metal-metal oxide pairs.³

If the energy dispersive detector (resolution of 3%) is replaced with a high-resolution wavelength dispersive spectrometer (resolution of 0.3%), the apparent anomaly is resolved. High-resolution measurements of the Ti $K\beta$ transition of Ti metal and TiO_2 , shown in Figure 2, reveal a series of satellite lines associated with the normal $K\beta$ diagram line at 4.93 keV. These satellite lines correspond to $K\beta$ X-rays emitted from configurations having multiple L vacancies. It can now be seen that the 200 eV energy shift is due to a centroid shift arising from the high cross section for multiple vacancies when fast, heavy-ions are used for excitation. Similarly, the 10 eV shift for TiO_2 is also due to a centroid shift. This shift is primarily the result of a change in the relative fluorescence yield of the satellite lines. Thus, the analytical advantage of HIXSE is that the yield distribution of the intense satellite lines is sensitive to the chemical environment of emitting ion.

Fig. 2. The corrected Ti $K\beta L^n$ satellite spectra of Ti metal (solid line) and TiO_2 (dashed line) produced by 36 MeV Cl ion excitation.

It should be noted that the Ti $K\beta L^n$ satellite spectra of Ti metal and TiO_2 have been corrected for projectile energy loss, concentration and mass absorption effects.

Correlation of these variations in the satellite yield or intensity distribution with parameters which characterize the chemical environment (effective charge and valence electron density) have been successful for a variety of second and third row elements.⁴ These correlations indicate that as the concentration or density of weakly bound valence electrons among the neighboring atoms increase, the relative satellite intensity distribution of the target ion shifts from higher-order to lower-order satellites. This effect is clearly seen in Figure 2 and Table 1 in which the valence electron density, D_v , (number of valence electrons/ $\text{\AA}^3$) of TiO_2 is greater than Ti. In a study of the chemical effects in the KL^n satellites of a series of sulfur compounds, it was demonstrated that the KL^5 configuration line is even more sensitive to changes in D_v .⁵

The best explanation for this phenomena is that prior to the emission of the K X-ray, the L vacancies are being partially refilled at a rate which is dependent on the valence-electron environment. Because the outer shell electrons are also removed during the collision process, the refilling of the L shell is believed to proceed through direct interatomic Auger transitions and by interatomic electron transfer to the valence level of the ion followed by rapid intra-atomic Auger cascading.^{4,6} The latter process is believed to be the dominant channel. 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.

Table 1. Bulk valence electron densities of Mo and Ti targets

Target	MoO ₂	Mo	MoSi ₂	MoTe ₂	TiO ₂	Ti
D _V (a)	0.548	0.387	0.350	0.241	0.514	0.226

(a) number of valence electrons/Å³

The utility of HIXSE as a chemical probe depends upon the range of elements for which this technique is sensitive, the degree of sensitivity and by its application to chemical and material problems. Because the sensitivity of the K α satellite lines to the chemical environment decreases as the number of shells between the L and valence level increases, the expansion of these studies to a broader range of elements depends upon the evaluation of chemical effects or shifts associated with other X-ray transitions. The L X-ray transition is an excellent candidate because the L X-ray satellites should be sensitive to the chemical effects of transition metal elements. Sensitivity to the chemical environment and bonding of transition metals is critical to the development of this method as a useful materials probe. Insights into the chemical sensitivity of HIXSE may also be gained by exploring a different transition.

In this report, improved high-resolution measurements of the L HIXSE spectra of a series of molybdenum alloys and compounds are presented. The preliminary results confirm the analysis and conclusions of previous studies⁷ and indicate a greater potential for chemical sensitivity.

EXPERIMENTAL METHODS

A beam of 36 MeV ³⁵Cl ions extracted from the Oak Ridge EN-tandem Van de Graaff accelerator was used to excite the L X-ray satellites of a series of Mo alloys and compounds. The X-ray spectra were obtained with the new, high-efficiency, high-resolution Bragg crystal spectrometer in a von Hamos geometry. The spectrometer, which has been described in detail elsewhere,⁸ uses a 10 cm cylindrically curved quartz (10 $\bar{1}$ 1) crystal with a 2d spacing of 6.687 Å and a radius of curvature of 25.4 cm to diffract the X-rays. The detector is a gas-flow, position-sensitive proportional counter (TEG-Knoxville, Tennessee) with a 10 cm active area. The energy resolution was 5 eV (fwhm) at 2.3 keV. Spectra were corrected for background signal and normalized. No other corrections have been applied. The Mo compounds were prepared as previously described.⁷ The Mo-Ti alloys were prepared by drop casting followed by homogenization at 1250°C for 16 hours. The samples were cut into 9 x 9 x 4 mm³ pieces and polished. After polishing, the samples were annealed at 400°C for 48 hours.

RESULTS AND DISCUSSION

The previous high-resolution (7 eV fwhm at 2.3 keV) study of the chemical effects in the Mo L HIXSE spectra, described in detail elsewhere,⁷ will be summarized here for comparison to the current work.

Fig. 3. The uncorrected Mo $L^N M^M$ satellite spectra of Mo metal (solid line) and MoO₂ (dashed line) produced by 36 MeV Cl ion excitation.

The L X-ray satellite spectra, unlike the K spectra, exhibit broad bands of unresolved $L^N M^M$ satellite lines. The shape and centroid position of the $L\alpha(2p_{3/2} \rightarrow 3d_{3/2,5/2})$ and $L\beta_1(2p_{1/2} \rightarrow 3d_{3/2})$ bands do, however, change with the chemical form of Mo observed. Using elemental Mo as a subtrahend, difference spectra were generated to enhance the variations. A linear relationship between the region of the difference spectra corresponding to the high-energy side of the $L\alpha$ band of a series of compounds and their bulk valence electron density was found. The correlation showed that as the bulk valence electron density (D_V) increases, the X-ray yield on the high-energy side of $L\alpha$ decreases. These results, along with theoretical calculations of $L^N M^M$ satellite energies, suggested that the high-energy side of the $L\alpha$ band corresponds to higher-order satellites and that these satellites exhibit a behavior similar to that observed for K transitions. A series of Mo-Ti bcc alloys were also examined. A linear correlation with D_V was shown to exist only for the $L\beta$ region of the spectra and the slope of the correlation was reversed. Similar results have been obtained for L HIXSE spectra of niobium and zirconium alloys and compounds.^{9,10}

The inability to observe the $L^N M^M$ configuration lines together with the apparent difference between alloys and compounds and $L\alpha$ and $L\beta$ transitions pointed to a need for a higher resolution device to study L HIXSE spectra. Figure 3 shows the uncorrected Mo $L^N M^M$ satellite spectra of elemental Mo and MoO₂ obtained with the higher-resolution, high-efficiency von Hamos spectrometer. The improved resolution (about 30%

greater than that obtained in the previous study) reveals L^{nM} configuration lines in the $L\alpha$ (channels: 400-850) and $L\beta$ (channels: 800-1200) bands. Because the Cl X-rays (produced in the target-projectile collisions) have an energy above the Mo L_3 and L_2 absorption edges, the sharp peaks at channels 420 and 810 correspond to the photo-excited $L\alpha$ and $L\beta_1$ diagram lines respectively. The partially resolved $L\alpha$ configuration lines of the compounds exhibit the same trend in the relative intensity as was observed for the KL^n lines of lower Z targets (4,5), i.e. as D_V increases the fluorescence yield of the higher-order satellites decreases relative to the lower-order. This similarity is clearly seen by comparing the metal-metal oxide spectra in Figures 2 and 3 and the values of D_V in Table 1. For the first time this effect, although less dramatic, is now seen in the $L\beta$ configuration lines. These results indicate that D_V is a reasonable chemical parameter to correlate to the L HIXSE spectral variations and support the proposed interatomic refilling mechanism. They also demonstrate a consistent behavior for the $K\alpha$, $K\beta$, $L\alpha$ and $L\beta$ transitions of compounds.

Uncorrected difference spectra, using elemental Mo as the subtrahend, were also examined. As was observed in the previous study, the region corresponding to the high-energy side, now more accurately to the higher-order L^{nM} configuration lines, enhance the same systematic change with D_V . For example, examination of Figure 4 and Table 1 shows that as D_V decreases from MoO_2 to $MoTe_2$, the higher-order $L\alpha$ satellite region (channels 700-900) mirrors that trend by changing from negative to nearly zero to positive. It can also be seen that the large oscillations in all the difference spectra correspond to the observed configuration lines. The uncorrected Mo-Ti alloy difference spectra (not shown) also exhibit the same trend in their difference spectra as was observed in the previous study. Additional analysis will be required to determine why HIXSE has a different and perhaps unique sensitivity to these materials.

The higher-resolution spectrometer also provides an opportunity to examine the L_3 absorption edge of Mo-bearing targets. Although the shift between Mo and many of the compounds can be readily observed (see Figure 3), differences between compounds having similar formal oxidation states, e.g. MoO_2 and $MoTe_2$ is more difficult (data not shown) to observe. HIXSE spectra, as seen in Figure 4, exhibit marked differences between these two compounds.

CONCLUSIONS AND FUTURE STUDIES

The higher-resolution data confirm the analysis and conclusions presented for the lower resolution L HIXSE experiments. The results also demonstrate a consistent chemical effect for the heavy-ion excited K and L X-ray satellites of the compounds. Finally, HIXSE appears to yield chemical information not easily observed by techniques such as ESCA or absorption edge measurements. Future work will involve correcting the data presented here for projectile energy loss, mass absorption and concentration effects. Attempts will be made to increase the sensitivity of the L HIXSE spectra in an analogous fashion to the K transition by correlating one or two configuration lines rather than all of the higher-order satellite lines. Alloy spectra will again be carefully analyzed for similarities to the spectra of compounds. Very-high-resolution studies (1 eV at 2.3 keV) will be attempted to develop a better understanding of the mechanism controlling HIXSE's ability to probe chemical effects and to improve the sensitivity of the analytical

technique. 'Very-high-resolution studies of the Ti $K\beta$ HIXSE spectra of a series of second-row transition metal-Ti binary alloys will also be attempted. Although the production cross section for this transition is small, the anticipated high chemical sensitivity may answer questions concerning HIXSE's ability to observe differences between similar alloys.

REFERENCES

1. J. B. Cross, R. Zeisler and E. A. Schweikert, High Energy Heavy-Ion Induced X-ray Emission Analysis, Nucl. Instrum. Meth. 142:111 (1977).
2. See for example: C. D. Wagner, W. M. Riggs, L. E. Davis, J. F. Moulder and G. E. Muilenberg, "Handbook of X-ray Photoelectron Spectroscopy," Perkin Elmer Corp., Eden Prairie (1979).
3. O. I. Sumbaev, The Effect of the Chemical Shift of the X-ray $K\alpha$ Lines in Heavy Atoms, Zh. Eksp. Teor. Fiz. 57:1716 (1969) [Sov. Phys.-JETP 30:927 (1970)].
4. R. L. Watson, A. K. Leeper, B. I. Sonobe, T. Chiao, and F. E. Jenson, Effect of Chemical Environment on the Intensities of $K\alpha$ X-ray Satellites Produced in Heavy-Ion Collisions, Phys. Rev. A 15:914 (1977).
5. C. R. Vane, L. D. Hulett, Jr., S. Kahane, F. D. McDaniel, W. T. Milner, G. D. O'Kelley, S. Raman, T. M. Rosseel, G. G. Slaughter, S. L. Varghese, and J. P. Young, Chemical Effects in High Resolution Sulfur K X-ray Spectra, Nucl. Instrum. Meth. 231 B3:88 (1984).
6. R. L. Watson, T. Chiao, and F. E. Jenson, Chemical Effect on $K\alpha$ X-ray Satellites: New Evidence for Interatomic Transitions, Phys. Rev. Lett. 35:254 (1975).
7. T. M. Rosseel, J. M. Dale, H. W. Dunn, L. D. Hulett, Jr., S. Kahane, H. F. Krause, S. Raman, G. G. Slaughter, C. R. Vane, and J. P. Young, Chemical Effects in L X-ray Satellites of Molybdenum Compounds and Alloys, Nucl. Instrum. Meth. 231 B3:94 (1984).
8. C. R. Vane, E. Kallne, J. Kallne, G. Morford, S. Raman, and M. S. Smith, Ultrahigh-Resolution Studies of Heavy-Ion-Induced X-ray Satellite Emission, Nucl. Instrum. Meth. B10/11:190 (1985).
9. T. M. Rosseel, J. M. Dale, L. D. Hulett, H. F. Krause, P. L. Pepmiller, S. Raman, C. R. Vane and J. P. Young, Effect of the Chemical Environment on the L and M Heavy-Ion-Induced X-ray Satellite Emission Spectra, Nucl. Instrum. Meth. B10/11:195 (1985).
10. T. M. Rosseel, J. M. Dale, L. D. Hulett, H. F. Krause, P. L. Pepmiller, S. Raman, C. R. Vane, J. P. Young, Chemical Effects on the L Heavy-Ion-Induced X-ray Satellite Emission (HIXSE) Spectra of Niobium Alloys and Compounds, Nucl. Instrum. Meth. A242:632 (1986).