L-subshell ionization of lutetium by \(^4\)He\(^{2+}\) ion bombardment

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Inner-shell ionization of materials was studied using particle-induced x-ray emission (PIXE) and Rutherford backscattering spectrometry (RBS). Measurements of the ionization cross-sections of lutetium were performed by impact of \(^4\)He\(^{2+}\) ions in the energy range 1.40–8.50 MeV. The experimental data were compared with the predictions of current theoretical models based on ion–atom collision resulting in inner-shell ionization. The discrepancy between theory and experiment at energies lower than about 5 MeV could be partially understood by incorporating intra-shell coupling that results in vacancy rearrangement among the three L-subshells. Copyright © 2002 John Wiley & Sons, Ltd.

INTRODUCTION

One of the fundamental parameters that is involved in the ion–atom collision process is inner-shell ionization cross-section that is needed for quantitative analysis in the particle-induced x-ray emission (PIXE) technique. PIXE is well established if protons (normally of energy of 2.5 MeV) are used as projectiles. Another analytical technique, Rutherford backscattering spectrometry (RBS), results from Coulomb scattering from atoms. RBS is well established if \(\alpha\)-particles (normally of energy 2 MeV) are used as projectiles. The simultaneous use of PIXE and RBS is desirable and offers many advantages for analysts. However, using an \(\alpha\)-particle beam of a few MeV simultaneously for PIXE and RBS is not well established because inner-shell ionization cross-sections for \(\alpha\)-particles, even at 2 MeV, are not known exactly, at least from the theoretical point of view.\(^1\)–\(^9\) Therefore, an understanding of the mechanism of inner-shell ionization when an \(\alpha\)-particle beam is used as a projectile would allow the simultaneous acquisition and quantitative analysis of PIXE and RBS spectra. The purpose of this work was to investigate the L-subshell ionization cross-sections of one of the rare earth elements, lutetium, for \(\alpha\)-particles with energies in the range 1.40–8.50 MeV. A comparison with current theoretical models is presented in an attempt to understand the ion–atom interaction process that results in inner-shell ionization.

EXPERIMENTAL

Data collection is based on simultaneous measurement of PIXE and RBS spectra. Details of the experimental procedure are discussed elsewhere.\(^10\) An ion beam from the accelerator is incident on the solid target and the backscattered particles are detected with a surface barrier (SB) detector while x-rays emitted from the sample are detected with a lithium-drifted silicon [Si(Li)] detector. The target consists of a thin film of LuF\(_3\) with nominal thickness 37.4 \(\mu\)g cm\(^{-2}\). Both PIXE and RBS spectra were collected simultaneously and stored on a floppy disk for further analysis off-line. The PIXANPC code was used for PIXE analysis\(^11\) and the RUMP code for RBS analysis.\(^12\) Experimental uncertainties arise from statistical uncertainties of x-ray and RBS yields (\(<5\%)\), efficiency-geometry factor (\(<7\%)\) and accuracy of the ion energy (\(<0.4\%)\). The final uncertainties in the ionization cross-sections were never better than 10% for transitions arising from initial vacancies in the L\(_1\)-subshell, 15% for transitions arising from L\(_2\) vacancies and 25% for transitions arising from L\(_3\) vacancies.

THEORETICAL PROCEDURES

PIXE analysis

When a beam of particles passes through a solid material, there is a probability that electrons from inner shells of atoms will be removed and vacancies will be created in subshells. The vacancies will be rapidly filled by electrons from higher shells with the result of emission of x-rays or Auger electrons. Measurement of the energy and intensity of the x-rays forms the basis for identifying and quantifying the sample elements by PIXE. The equation that relates different physical parameters in PIXE is given for the case of thin films in the following standard form:\(^13\)\(^14\)

\[
Y^*_i = \Omega QC\epsilon \sigma^e_i \tag{1}
\]

where \(Y^*_i\) is the x-ray yield of the L\(_i\)-subshell (\(i = 1, 2\) or 3), \(\Omega\) is the solid angle subtended by the Si(Li) detector, \(Q\) is the total charge representing in our case the number of \(\alpha\)-particles with \(<2\) MeV energy, \(\epsilon\) is the Si(Li) detector efficiency and \(\sigma^e_i\) is x-ray production cross-section of the L\(_i\)-subshell. The two quantities which are difficult to measure are \(Q\) and \(C\). To measure \(Q\), one needs a totally isolated system which...
is subjected to environmental effects. The concentration C is affected greatly by the fluence of the ion beam and the accompanying heating effects.

**RBS analysis**

In RBS, as the incident ions enter the surface, a small fraction of them collide with atoms and suffer classical elastic backscattering. The ions are emitted from the surface with an energy lower than the incident energy and characteristic of the target atom. In this manner, RBS provides elemental analysis and depth distribution information. The equation that relates different physical parameters in RBS is given by the standard relation\(^2\)

\[
Y_R = \Omega QC \sigma_R
\]  

(2)

where \(Y_R\) is the backscattering yield which can be measured from the RBS spectrum, \(\Omega\) is the solid angle subtended by the SB detector and \(\sigma_R\) is differential backscattering cross-section.

**Method of calculations**

The backscattering problem can be treated classically and the kinematic equations give solutions which are known exactly with no approximations involved. On the other hand, \(L_2\)-subshell ionization process has to be treated quantum mechanically with some approximations involved. The cross-section for atomic inner-shell ionization by accelerated positive ions is most commonly described by the plane wave Born approximation (PWBA) with corrections for energy loss (E), Coulomb deflection (C) of the ion’s trajectory, perturbed stationary state correction (PSS) for ion-induced binding and polarization effects, and relativistic effects (R). The result is the theory known as ECPSSR theory.\(^6\)

Dividing Eqn (1) by Eqn (2), one can eliminate the troublesome parameters \(Q\) and \(C\). After rearranging the parameters, we have

\[
\sigma_i^* = \left( \frac{\omega}{\epsilon} \right) \left( \frac{Y^4}{Y_R} \right) \sigma_R
\]  

(3)

The parameters on the right-hand side of Eqn (3) can be either measured (\(\omega, \epsilon, \Omega, Y^4, Y_R\)) or calculated exactly (\(\sigma_R\)). Details of the measurement of \(\Omega/\epsilon\) were discussed in detail in a previous publication.\(^7\) Hence x-ray production cross-sections can be determined using Eqn (3). To obtain the experimental ionization cross-sections \(\sigma_i^*\) from the measured x-ray production cross-sections \(\sigma_i^\prime\), the following standard equations were used: \(^18\)

\[
\begin{align*}
\sigma_1^1 &= \sigma_2^1 \\
\sigma_2^1 &= \sigma_2^2 - f_{12} \sigma_1^1 \\
\sigma_3^1 &= \sigma_2^3 - f_{23} \sigma_1^3 - (f_{13} + f_{12} f_{23}) \sigma_1^1
\end{align*}
\]  

(4)

where \(\omega_i\) is the \(L_i\)-subshell fluorescence yield and \(f_{ij}\) is the Coster–Kronig transition probability between the \(L_i\) and \(L_j\) subshells.\(^19\) The experimental ionization cross-sections were then compared with the theoretical values of the ECPSSR theory using the program ISICS of Liu and Cipolla.\(^20\)

The effect of collision-induced intra-shell transitions was included in the ECPSSR theory to give ECPSSR-IS predictions.\(^8\) Further corrections were applied to the ECPSSR-IS theory by incorporating the binding energy of the united atom as described by Sarkadi and Mukoyama\(^8\) and known as the UA correction. One expects an increase in the binding energy that should not exceed the binding energy of the united atom (target atom + incident ion). The result of applying the IS correction followed by the UA correction gives the ECPSSR-IS-UA theoretical predictions.

**RESULTS AND DISCUSSION**

Experimental L-shell ionization cross-sections versus the projectile energy and the corresponding theoretical predictions of the ECPSSR theory are shown in Fig. 1. For the \(L_1\)-subshell the theory seems to underestimate slightly the experimental values for projectile energy above about 5 MeV. Below this energy the ECPSSR theory overestimates the experimental values.\(^1–9\) Over-all, satisfactory agreement between theory and experiment appears at bombarding energies higher than 5 MeV. A possible conclusion from the above discussion is that the \(L_2\)- and \(L_3\)-subshell ionization cross-sections increase at the expense of the \(L_1\)-subshell ionization cross-section. This is illustrated in Fig. 1, which shows also a plot of the total ionization cross-sections versus energy of \(^4\)He\(^{2+}\) ions. It can be seen that there is good agreement between them at almost all energies considered in this work. This can be explained in terms of the effect of the collision-induced intra-shell transition effect and the electronic binding correction introduced by Sarkadi and Mukoyama.\(^5\) At low energies, the intra-shell effect becomes much larger for the \(L_2\)-subshell than the \(L_1\)-subshell since the response time for electrons in the \(L_2\)-subshell is longer than that in the \(L_1\)-subshell. This can suppress the ionization

**Figure 1.** \(L_1, L_2, L_3\) and \(L_T\) ionization cross-sections for Lu measured as a function of \(^4\)He\(^{2+}\) energy. The ECPSSR theoretical predictions are represented by the solid curve.
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cross-section of L₂-subshell significantly. The binding effect becomes negligible at high energies when the collision time is very short compared with the electronic response time in any particular subshell. This argument follows reasonably well from the fact that the ECPSSR theory is based on solving the Schrödinger equation for the ion–atom collision process in the PWBA with screened hydrogen-like wavefunctions where two criteria must be valid, namely \( Z_1 \ll Z_2 \) and \( v_1 \gg v_2 \), where \( Z_1 \) and \( Z_2 \) refer to the projectile and target atomic numbers and \( v_1 \) and \( v_2 \) are the projectile and target-atom electron velocities, respectively.

As shown by Sarkadi and Mukoyama, the ionization process cannot be treated independently for individual L-subshells, because the projectile can induce secondary intra-shell (IS) transitions between different subshells. When this effect is calculated we obtain the ECPSSR-IS values.

The ratio \( \sigma_1/\sigma_i \) of ionization cross-sections is particularly sensitive to the shape of the excitation functions of the corresponding subshells and highlights regions of disagreement not obvious from a comparison of absolute values. This offers a good test of the theoretical predictions. The radial wavefunction of the L₁-subshell is particularly interesting since it has a nodal structure that falls in the region of interest in the present context and it has two peaks. In this case, the most probable value of average radius of the orbit corresponds to that value which has the highest probability density. An electron in the 2s state would be much further from the nucleus (on average) than an electron in the 1s state and slightly further from an electron in the 2p state. It is believed that this effect is reflected on cross-section values.

Figures 2, 3 and 4 show the ratios \( \sigma_1/\sigma_i \), \( \sigma_1/\sigma_2 \) and \( \sigma_2/\sigma_i \) respectively, versus the energy of the \( ^4\text{He}^{2+} \) ion beam. Starting with Fig. 2, it can be seen that the qualitative and quantitative agreement between the ECPSSR curve and the experimental data is satisfactory except for the low-energy region below 5 MeV. The predictions of the ECPSSR theory seem to overestimate the experimental data at energies below 5 MeV. A similar trend was observed for the dependence of the \( \sigma_1/\sigma_i \) ratio on the energy of \( ^4\text{He}^{2+} \) ion beam (Fig. 3), except that the discrepancies are larger than in the previous case. The variation of \( \sigma_2/\sigma_1 \) with the energy of the \( ^4\text{He}^{2+} \) ion beam is shown in Fig. 4. The theory seems to underestimate the experimental data at all energies considered. The discrepancies are even greater at low energies. The results overall agree with our previous work and the general trend observed in the work of Sokhi and Crumpton for Yb bombardment with protons and the work of Cuzzocrea et al. for Te bombardment with \( ^4\text{He} \) ions. Careful examination of Figs 2 and 3 shows that the theory can in principle match the experiment if L₂- and L₃-subshell ionization cross-sections increase at the expense of L₁-subshell ionization cross-sections, especially at energies lower than 5 MeV. On the other hand, Fig. 4 might indicate that, from the theoretical point of view, the L₂-subshell should increase at a rate higher than that of the L₃-subshell in order for the theoretical ratio to shift up and match the experiment. This result is in complete agreement with the work of Cai et al. on L-subshell ionization of Lu by 1.5–4.5 MeV alpha particles.

The above argument implies that the inclusion of intra-shell effects in the ECPSSR theory leading to ECPSSR-IS predictions might be a step in the correct direction. The results are again shown in Figs 2–4. In Fig. 2, the inclusion of

the IS correction certainly improves the agreement between theory and experiment, especially at low energies below 5 MeV. There is still, however, a slight overestimation of the cross-sections by the ECPSSR-IS theory at energies less than about 5 MeV.

In Fig. 2, the variation of $\sigma_1/\sigma_2$ with the energy of the projectile when the ECPSSR-IS theory is compared with experimental data is very similar to the previous case. The theoretical ratio becomes much closer to the experimental values. For the $\sigma_1^L/\sigma_2^L$ ratio versus energy (Fig. 4), the ratio changes drastically in the low energy region below about 5 MeV when the IS correction is included in the theoretical calculations. In other words, the ratio now agrees much better with the theory but there is still an overall underestimation of the cross-section ratio by the theory.

The inclusion of the UA correction in the ECPSSR-IS theory gives ECPSSR-IS-UA theory. This inclusion does not seem to be important in this case of Lu ionization by $^4$He$^{2+}$ ions. From Figs 2–4, it is obvious that little difference is observed between the ECPSSR-IS and ECPSSR-IS-UA predictions.

In conclusion, we have presented a case study of Lu L-subshell ionization cross-section measurements by bombardment with $^4$He$^{2+}$ ions of energies in the range 1.40–8.50 MeV where the $L_1$-subshell electronic wavefunction has a node in its structure. Comparison of the ionization cross-section ratios $\sigma_1/\sigma_2$, $\sigma_1^L/\sigma_2^L$ and $\sigma_1^L/\sigma_2^L$ with the ECPSSR theory revealed serious discrepancies in the low-energy region which agrees with similar observations reported in the literature. Coupled-state calculations that account for intra-subshell transitions give better agreement between theory and experiment. On the other hand, the inclusion of modifications of binding energy in the united atom picture gives practically no difference in the calculated ECPSSR-IS predictions. Coupling effects are perhaps not the sole explanation of known discrepancies between theory and measurements. The results are believed to provide a useful input for further theoretical studies on the inner-shell ionization mechanism. This is very important in the application of the named techniques for material analysis and characterization.

REFERENCES