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Multiple ionization X-ray satellites of magnesium, aluminum and silicon in alpha particle PIXE

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A R T I C L E I N F O

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A B S T R A C T

Wavelength-dispersive spectroscopy was used to study the multiple ionization satellites in the K X-ray spectra of magnesium, aluminum and silicon bombarded by alpha particles having energies of 3, 4 and 5 MeV. The measured energy shifts and intensities relative to the diagram lines of the groups with one, two and three L-shell vacancies were extracted from the spectra. These results compare well with the values in an interim database which was recently assembled from the limited existing literature. The present work is the first step in refining this database so that it may be used to improve the accuracy of PIXE analysis using alpha particle beams, including the PIXE mode of the Mars alpha particle X-ray spectrometers. The effects of oxide bonding are also determined and compared to those observed when excitation is effected by photons and by electrons.

1. Introduction

1.1. Background

The spectra acquired by the silicon drift detectors (SDD) within the alpha particle X-ray spectrometers (APXS) on the Mars rovers Spirit, Opportunity and Curiosity are generated by particle-induced X-ray emission and X-ray fluorescence. This is achieved through exposure of the sample to a combined flux of 5 MeV alpha particles and plutonium L X-rays emitted from a ring of six ^{244}Cm sources [1]. For light elements extending up to titanium, the alpha particles generate the majority of the observed X-ray signal. Recent work [2,3] has shown that the quality of non-linear least-squares fits to APXS spectra is significantly improved by accounting in a systematic manner for two un-related effects. The first of these is instrumental non-linearity, which manifests itself as a departure in the X-ray energy region below ~5 keV from the linear channel-energy relationship. We have found that, in a given SDD temperature range, this effect increases linearly as the X-ray energy decreases, enabling us to develop a systematic correction algorithm for that temperature range. The second is the presence of multiple ionization (MI) satellites. While these are almost negligible contributors in particle-induced X-ray emission (PIXE) spectra generated by protons, this not the case when alpha particles are used. As an example, for the light elements Z = 11…14 the intensity of the energy-shifted alpha-induced satellite KL^1 arising from a single L spectator vacancy is in approximately 1:1 ratio with the diagram line (KL^0) intensity; and the KL^2 and KL^3 features have double and triple energy shifts coupled with significant intensities.

To characterize these satellites, high-resolution wavelength-dispersive spectroscopy is mandatory. To exemplify such spectra at the outset, our measured profiles for the silicon Kα line in the element and its oxide are displayed in Fig. 1. Both spectra were produced using 3 MeV alpha particle excitation. Principal diagram and multi-vacancy lines have been indicated using the classic Seigbahn notation. The grouping of individual lines goes as KL^0 ($K\alpha_1$, $K\alpha_2$), KL^1 ($K\alpha'$, $K\alpha_{3s}$, $K\alpha_3$, $K\alpha_3'$, $K\alpha_4$), KL^2 ($K\alpha_8$, $K\alpha_5$, $K\alpha_5'$, $K\alpha_7$, $K\alpha_6$) and KL^3 ($K\alpha_9$, $K\alpha_{11}$, $K\alpha_{10}$). The fitting of such spectra to appropriate models will be discussed later in this paper.

MI satellites are not catered for in the widely-used GUPIX software package [4] for accelerator-based PIXE analysis. Their inclusion would improve the accuracy of alpha particle PIXE, which is an attractive prospect since it offers the advantage of conducting PIXE and Rutherford backscattering analysis with high accuracy on a given specimen. To pursue this goal, a database of satellite energies and intensities

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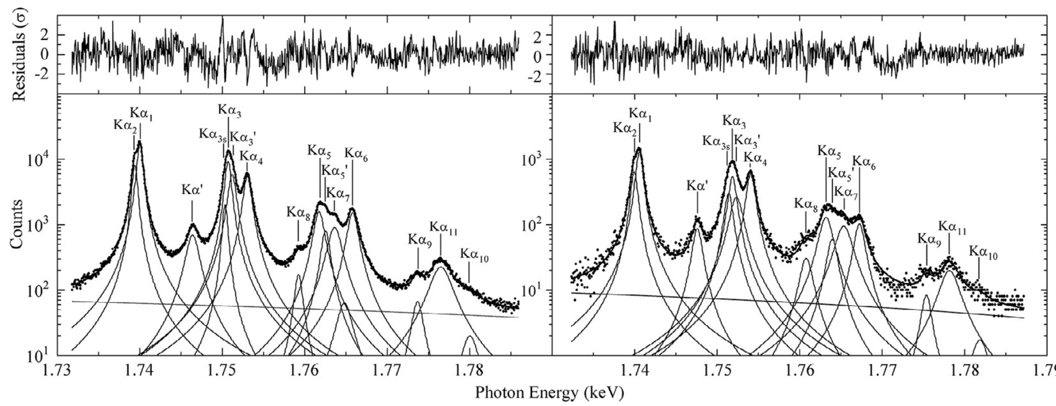

Fig. 1. Wavelength dispersive spectrum of 3 MeV alpha particle bombardment of Si (left panel) and SiO_2 (right panel) fitted using Lorentzian functions for line descriptions, sitting on a flat background (not shown). Fit residuals indicating goodness of fit are included in the top panel. Lower panels are plotted on a log-linear scale.

resulting from alpha particle excitation has been assembled from the literature by author Heirwegh [2]. That task drew on a rather small number of data sources, and interpolation and extrapolation were necessary. The resulting database, whose development is summarized in Section 2 below, should therefore be regarded as a temporary tool. In this paper we report our first attempt to improve it, focussing on the elements magnesium, aluminum and silicon.

1.2. Multi-vacancy X-ray satellites in light elements

The hypothesis that the multi-vacancy state was the source of X-ray satellite lines was made nearly a century ago by Wenzel [5], and has been confirmed primarily through photon and electron ionization work involving wavelength dispersive spectroscopy (WDS) techniques. The focus of most work is measurement of the intensity ratio between the KL^1 satellite group and the KL^0 diagram line. Values of this ratio spanning the past ~50 years are collected in Table 1. The results in each section are sequenced in time to assist the reader in assessing the impact of both improved technology and improved sophistication in spectrum fitting. In most but not all cases, small corrections were applied for detector window absorption and varying reflectivity of the diffraction crystal. In a minority of cases small corrections for target self-absorption were effected. We do not claim completeness, but there are sufficient results to identify trends. We also include some results for the oxides of the three elements and a few results using proton and alpha particle excitation.

In photon work the satellites are attributed to shake processes only and their overall intensities in our three elements are small (~10–15%) relative to the diagram emission line. For all three elements of interest here, the photon excitation work of Mauron et al. [10], using a Von Hamos spectrometer, gives smaller KL^1/KL^0 ratios than all the earlier photon references in Table 1. Although results from both photon and electron excitation exhibit considerable scatter, the trend is clearly an increased satellite intensity for the electron case. The additional contribution in electron excitation comes from Coulomb excitation of multiple vacancies. Several of the electron works in Table 1 have shown that energy at least twice the K binding energy of the target atom is required to ensure that the full satellite yield is attained.

Only half of the studies in Table 1 compare results for the element and its oxide, and only seven of these provide error estimates. Nevertheless, these data are consistent in suggesting that the KL^1/KL^0 ratio increases by ~10% in the oxide state. A small minority of the references of Table 1 also give results for the intensity ratio $K\alpha_4/K\alpha_3$ within the KL^1 satellite group. Going from element to oxide this ratio increases by a factor in the range 1.4–3.4. Clearly, this ratio is much more sensitive to oxidation, and will therefore be examined in what follows for the case of alpha particle excitation.

Table 1
Measured KL^1 satellite intensity relative to the $K\alpha_{1,2}$ (KL^0) diagram line intensity. Excitation is by X-rays (X), electrons (e), hydrogen ions (H), helium ions (He). The symbol c indicates that corrections were made for X-ray absorption in windows and for variation in reflectivity of the diffracting crystal; these effects were generally very small.

Target and excitation mode	Excitation Details	Source	KL^1/KL^0 Element	KL^1/KL^0 Oxide
Mg (X)	Cr K c	[6]	0.140 ± 0.003	0.158 ± 0.002
	Mo L	[7]	0.14	
	Rh L c	[8]	0.139 ± 0.006	
	Rh L	[9]	0.139 ± 0.008	0.150 ± 0.010
	Cr K c	[10]	0.114 ± 0.001	
Mg (e)	4–5 keV	[11]	0.187	0.18
	3 keV	[7]	0.15	
	6 keV c	[12]	0.155 ± 0.003	
	12 keV c	[13]	0.161 ± 0.007	
Al (X)	Cr K c	[6]	0.108 ± 0.002	0.123 ± 0.002
	Ag L	[7]	0.1	
	Cr K c	[10]	0.078 ± 0.008	
	Rh L c	[14]	0.099 ± 0.009	0.114 ± 0.010
Al (e)	4–5 keV	[15]	0.13	
	3.5 keV	[7]	0.1	
	6–12 keV c	[12]	0.117	
	12 keV	[13]	0.102 ± 0.005	
Al (H)	1.7 MeV/amu	[16]	0.165	
Al (He)		[16]	0.429	
Si (X)	Cr K c	[6]	0.078 ± 0.003	0.090 ± 0.004
	Cr K	[17]	0.093	0.103
	Rh L	[18]	0.089 ± 0.002	0.104 ± 0.002
	Cr K c	[10]	0.0572 ± 0.0003	
	Ag L c	[19]	0.079 ± 0.006	0.089 ± 0.007
Si (e)	6–8 keV	[20]	0.105	0.106
	12 keV	[21]	0.114	
Si (H)	1 MeV c	[22]	0.186 ± 0.01	
Si (H)	2 MeV c	[22]	0.132 ± 0.007	
Si (H)	3 MeV c	[22]	0.085 ± 0.008	
Si (He)	5.4 MeV c	[23]	0.733	0.679

Intense study of ion beam induced satellites commenced in the 1970s, a major focus being on the dramatic changes in the satellite spectra with increasing projectile atomic number. With ions heavier than helium, the predominant intensity in the K X-ray spectrum no longer lies within the KL^0 ($K\alpha_{1,2}$) feature. Instead, the KL^i satellites dominate the spectrum, exhibiting a binomial distribution of intensity [24]. The complexity of these spectra is one main reason why heavy ions have seen little practical application in the PIXE field. (The other reason is that as the mass of the exciting ion increases, significant departures appear between measured ionization cross-sections and the predictions of the ECPSSR theory [25].) Much less attention was paid to