Bimetallic cluster cations ejected from a liquid metal ion source: Li–Na and Li–Mg

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Abstract. Cluster ions of alloys (Li–Na, Li–Mg) have been produced by a liquid metal ion source (LMIS), and analyzed by mass spectrometry. For the Li–Na system, bimetallic clusters with various compositions were formed, and dominant bimetallic species were Na₂Li⁺, NaLi⁺, NaLi₂⁺ and NaLi₈⁺ with this sequence of ion intensity. These clusters are systems containing 2 or 8 valence electrons except for NaLi⁺. For the Li–Mg, observed bimetallic clusters were limited to only three species (MgLi⁺, MgLi₂⁺ and Mg₂Li⁺), but unexpectedly small multiply charged homonuclear clusters, Mg₂⁺ and Mg₃⁺, were observed.

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1. Introduction

While most experiments on gas phase clusters are concerned with neutrals, studies on charged clusters also offer important knowledge. First, since mass spectra obtained by ionization of neutral clusters are a convolution of various factors such as size distribution of original neutral clusters, size-dependent ionization cross-section and fragmentation, the interpretation of the mass spectra are generally intractable. On the other hand, it is usually accepted that mass spectra of “born ionized” clusters in a liquid metal ion source (LMIS) technique or secondary ion mass spectrometry (SIMS) show rather straightforward correspondence with the relative stability of ionized clusters [1]. Secondly, the ionization mechanism in LMIS, which is now under scientific debate though the dominant process is believed to be electron tunneling, is quite different from that in photoionization or electron bombardment of neutrals. Therefore, studies of cluster ions ejected from LMIS may provide new insight into the electronic properties of clusters.

There has been extensive experimental [2–4] and theoretical work [5, 6] on Ia–Ia and Ia–IIa bimetallic clusters such as LiₓNaᵧ, NaₓMg and KₓMg which intends to test the validity of the jellium model [7] for explaining stability and other properties of metal clusters. However, the cluster source used in the work referred above is limited to the supersonic expansion. In the present study we have produced bimetallic clusters from alloy (Li–Na, Li–Mg) LMIS. Attention is focused on magic numbers of bimetallic Li–Na clusters and to multiply charged small Mg clusters.

2. Experimental

The LMIS used in the present experiment is equipped with a closed-type reservoir for source material and with a needle emitter which are heated by electron bombardment. The needle can be moved back and forth relative to the reservoir from outside of vacuum [8]. Baking the needle tip in cooperation with the mechanical movement of the needle facilitates wetting the tip with liquid metal.

Mixtures of small pieces (ca. 1 mm³ cubes) of constituent metals (Li and Na, Li and Mg) were used as source materials. A piece of iron or tungsten wire with diameter of 0.5 mm was used as a needle emitter which was sharpened to a tip radius of several micrometers by conventional electrochemical etching.

The mass distribution of ions ejected from the tip was measured by using a single focusing magnetic analyzer with an orbital radius of 20 cm.

3. Results and discussion

3.1. Li–Na

Figure 1 shows a mass spectrum of ions ejected from a Li–Na (ca. 50 at.% alloy LMIS for an ion acceleration voltage $V_{acc}$ of 5.3 kV and a total emission current $I_t$ of...
12 \mu A. Not only bimetallic clusters with various compositions but also homonuclear clusters are observed. The relative abundance of homonuclear ones, Na\textsubscript{m}\textsuperscript{+} and Li\textsubscript{n}\textsuperscript{+}, is lower in this case than that obtained from respective pure metals [9]. Magic numbers observed in a series of homonuclear clusters are the same as those for the respective pure metal LMIS's [9].

Dominant species of bimetallic clusters are Na\textsubscript{2}Li\textsuperscript{+}, NaLi\textsuperscript{+}, NaLi\textsubscript{2}\textsuperscript{+} and NaLi\textsubscript{s}\textsuperscript{+} with this sequence of ion intensity. These clusters are systems containing 2 or 8 valence electrons except for NaLi\textsuperscript{+}. Since the valence-electron energy levels of Li and Na atoms are very close to each other (5.390 eV for Li, 5.138 eV for Na), the valence electrons in the bimetallic clusters are delocalized [6]. Therefore, the high stability of the bimetallic clusters with 2 and 8 valence electrons may also be explained by the electronic shell structure [7].

Most of the other bimetallic clusters can be classified into two series, Na\textsubscript{k}Li\textsuperscript{+} and Na\textsubscript{k-1}Li\textsubscript{2}\textsuperscript{+}. Their relative ion intensity (intensity of NaLi\textsuperscript{+} is normalized to unity) are plotted against the number of valence electrons, k, in Fig. 2. The intensity of NaLi\textsubscript{s}\textsuperscript{+} is also shown in the figure. The intensity variations of the two series show a similar pattern to each other; cluster cations containing even number of valence electrons give local maxima or step edges (even-odd oscillation). This seems to indicate that the number of valence electrons in a cluster is a dominant factor governing the stability of the bimetallic alkali clusters as it is for the homoatomic alkali clusters [9, 10]. However, strong dependence of ion intensity on the composition of clusters is also found; NaLi\textsubscript{s}\textsuperscript{+} has extraordinarily high intensity among the clusters containing the same number of valence electrons (see Fig. 2). The origin of the high abundance of NaLi\textsubscript{s}\textsuperscript{+}, including the formation kinetics and thermodynamic stability, is an open question.

### 3.2. Li–Mg

Figure 3 shows a mass spectrum of ions ejected from a Li–Mg (ca. 10 at.%) alloy LMIS at \( V_{acc} = 7.7 \) kV and \( I_t = 15 \mu A \). Here, observation of doubly charged Mg dimer and trimer is of main interest since bimetallic clusters detected were only MgLi\textsuperscript{+}, MgLi\textsubscript{2}\textsuperscript{+} and Mg\textsubscript{2}Li\textsuperscript{+}. Detailed description on singly charged homoatomic and bimetallic clusters as well as the doubly charged Mg clusters will appear elsewhere [11].

Peaks with half-integer mass-to-charge ratio, \( m/z = 24.5 \) and 25.5 are observed. This indicates the presence of doubly charged Mg dimers, since Mg has three isotopes, \( ^{24}\text{Mg} \) (natural abundance, 78.7%), \( ^{25}\text{Mg} \) (10.1%) and \( ^{26}\text{Mg} \) (11.2%). To measure the intensity of the dimers quantitatively, mass patterns composed of Mg\textsuperscript{+} and Mg\textsubscript{2}\textsuperscript{+} were calculated under an assumption that the relative intensity of isotope peaks were equal to the natural abundance. The calculated pattern reproduced