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Isotopic anomaly in dimer emission from alloy liquid-metal-ion-source mass spectroscopy

Jean Van de Walle, René-Jean Tarento, and Pierre Joyes
Laboratoire de Physique des Solides, Université Paris-Sud, 91405 Orsay, France

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In a pure copper liquid-metal-ion source (LMIS) the three Cu_2^+ isotopes are emitted with intensities close to the natural abundances while for a $\mathrm{Au}_{0.5}\mathrm{Cu}_{0.5}$ LMIS we only observe the $^{63}\mathrm{Cu}^{63}\mathrm{Cu}^+$ and $^{65}\mathrm{Cu}^{65}\mathrm{Cu}^+$ homoisotopic species. A similar phenomenon appears for the emission of Ge_2^+ from pure germanium compared to a $\mathrm{Au}_{0.73}\mathrm{Ge}_{0.27}$ alloy. We observe that the emission of the heteroisotopes is strongly reduced in the alloy case. We propose the following interpretation. In the electric-field zone close to the surface the two atoms of the heteroisotopic ion have different trajectories. As a consequence the molecular M_2^+ ion (M=Cu or Ge) is deformed and an electronic excitation appears which makes easier the tunneling of the outer electron from M_2^+ to the bulk available levels of the liquid metal or alloy. Moreover, the electronic structure of the alloy is such that the tunneling effect is easier than for the metal (for example, the work function is larger for $\mathrm{Au}_{0.5}\mathrm{Cu}_{0.5}$ than for Cu). Then, the absence or reduction of the Cu_2^+ or Ge_2^+ heteroisotope intensities in alloy LMIS would be due to the conjunction of two effects: presence of an electronic excitation specific to heteroisotopes and easier tunneling effect for alloys. [S0163-1829(96)04425-6]

I. INTRODUCTION

The liquid-metal-ion-source (LMIS) technique provides intense beams of mono- and polyatomic ions. For this reason the method has received industrial applications, for example it is used as primary beam in microlithography,[1] doping of semiconductors[2] or for elaborating microcircuits.[3]

Let us briefly describe the main features of the experiment. A solid tip made of a refractory metal (for example, W) is wetted by a melted metal M (alloys can also be used) and a strong electric field (of the order of 1 V/Å) extracts mono- and polyatomic M_n^p ions from the Taylor cone formed by the liquid metal. The sign of the p charge depends on the direction of the electric field, it is positive if the field is directed outward the tip.

Here we want to report on a surprising isotopic anomaly appearing in the M_2^+ dimers when they are emitted by an alloy LMIS. We will use Au_xM_{1-x} alloys which have already been studied by the LMIS technique[4,5] and the M elements will be Cu and Ge whose natural abundances are ^{63}Cu: 69.09%, ^{65}Cu:30.91%, ^{70}Ge:20.52%; ^{72}Ge:27.43%; ^{73}Ge:7.76%; ^{74}Ge:36.54%; ^{76}Ge:7.76%.

It is worth noticing that the subject of isotopic anomalies in the emission of particles from surfaces has already been widely studied in the case of secondary ion mass spectrometry (SIMS) experiments. For example, the emission of monoatomic ions exhibits a systematic decrease of the heaviest isotope intensity with respect to the natural abundances. This effect can be explained by the ionization mechanism since the ionization probability is larger at high emission velocity and the emission velocity smaller for the heaviest isotopes.[6,7] Another kind of isotopic anomaly has been observed for neutral atoms sputtered from a target, the phenomenon is called isotopic fractionation.[8] The effect has a transient character. Immediately after the bombardment an increase of the lightest isotope emission is observed. As a consequence the target is enriched in the heaviest element whose current progressively increases until its value becomes proportional to its natural abundancy; then, a stationary regime is reached. The transient effect is explained by collision cascade theories.[8,9]

Polyatomic ions observed by the SIMS technique also exhibit isotopic anomalies, for example for Cu_n^+.[10,11] To our knowledge, this phenomenon is not yet understood.

II. EXPERIMENTAL LMIS RESULTS

The observed effect can be summarized as follows. When studying the M_2^+ emission (M=Cu, Ge) from the pure M LMIS all the isotopes appear with relative intensities close to the natural abundances. On the contrary, when a Au_xM_{1-x} alloy is used the M_2^+ heteroisotopes completely disappear or have intensities much reduced with respect to the pure M case.

Our results are given for copper in Table I. For pure copper all the isotopes are present, while for $\mathrm{Au}_{0.5}\mathrm{Cu}_{0.5}$ only the homoisotopes $^{63}\mathrm{Cu}^{63}\mathrm{Cu}^+$ and $^{65}\mathrm{Cu}^{65}\mathrm{Cu}^+$ are present. We cannot report on other isotopic anomalies in the $\mathrm{Au}_{0.5}\mathrm{Cu}_{0.5}$

TABLE I. Measured currents for Cu_2^+ ions (arbitrary unit) in the case of a pure copper LMIS (first line) and a $\mathrm{Au}_{0.5}\mathrm{Cu}_{0.5}$ alloy (third line). The second and fourth lines are the first and third line values normalized by dividing by the lightest isotope value. The absolute values of the first and third lines cannot be compared since the tips are not the same and therefore the experimental conditions are different. The fifth line gives the normalized natural abundances.

Cu_2^+	$^{63}\mathrm{Cu}^{63}\mathrm{Cu}^+$	$^{63}\mathrm{Cu}^{65}\mathrm{Cu}^+$	$^{65}\mathrm{Cu}^{65}\mathrm{Cu}^+$
Copper	2300	2300	1400
Norm	1	1	0.61
Alloy	2660	0	1250
Norm.	1	0	0.47
Stat.	1	0.83	0.172

TABLE II. Measured currents for Cu_3^+ ions (arbitrary unit) in the case of a pure copper LMIS (first line). The second line gives the normalized currents, the third line gives the normalized natural abundances (for the normalization see the Table I caption).

Cu_3^+	$^{63}Cu_3^+$	$^{63}Cu_2{}^{65}Cu^+$	$^{63}Cu{}^{65}Cu_2^+$	$^{65}Cu_3^+$
Copper	1200	2200	800	150
Norm.	1	1.84	0.67	0.125
Stat.	1	1.25	0.52	0.071

mass spectrum because the Cu_3^+ peaks are superimposed with a wide Au^+ peak and the Cu_n^+ with $n \geqslant 4$ have too weak intensities. However we may notice that for the pure copper LMIS the four Cu_3^+ isotopes have intensities which roughly correspond to the natural abundances (Table II).

The precision of our measurements is only of the order of 30%. This lack of precision is usual in the LMIS measurements. It is certainly due to the instabilities of the emission zone whose geometrical structure is not reproducible between two experiments and, even, can change in the course of an experiment. We will come back to the precision of our experimental data at the end of this chapter, in any case the previous remark prevents us to consider as significant small deviations of the measured values with respect to the natural abundances. However, the large $^{65}Cu{}^{65}Cu^+$ intensity observed for pure copper as well as for the alloy LMIS (Table I) can be considered as significant and would deserve to be physically understood. In this paper, we will concentrate on the heteroisotope effect and will examine the previous homoisotope effect in another work.

Let us note that we have not taken into account the possible presence in the mass spectrum of Cu_{2n}^{2+} species which would superimpose with Cu_n^+ ions. This is justified here since, due to Coulombic explosion, the smallest doubly charged ion is Cu_3^{2+} (Ref. 12) and therefore the Cu_4^{2+} ion which is close to this limit has a small stability and a small probability to be formed.

The achievement of a Ge LMIS is somewhat easier and its stability better than a Cu LMIS. However, as there are now 15 Ge_2^+ isotopes the relative abundances are smaller and, as a consequence, the precision of our measurements is not better than for copper (∼30%). Our results for the pure Ge LMIS are given in Table III. We first notice that all the 11 natural peaks (some different isotopes correspond to the same mass which explains the reduction from 15 isotopes to 11 peaks) are observed. They can be grouped into three sets of values according to their intensities high, medium or low which gives respectively: high: {146,144,148,142}, medium: {150,145,147,:140,143,149}, low {152} (the values have been ordered by decreasing intensity inside each set). If we make the same classification for natural abundances (see Table III) we obtain similar results, in particular the first set is exactly the same for composition and order. There are only small changes concerning medium and low values for example the 149 peak would now belong to the third set instead of the second one. The main difference is that the experimental relative intensities are obtained in a narrower interval: [2; 0.21] instead of [5.8; 0.14]. As a conclusion, one may say that there is a global agreement between the observed and natural abundances for a pure Ge LMIS.

The alloy study has been performed on the $Au_{0.73}Ge_{0.27}$ alloy that we have already studied in another work.[4] The Ge_2^+ results are completely different, only four important peaks are present (140,144,146,148) with almost equal intensities (Table III). For the other masses the precision of our results does not allow to extract the information from the noise present in the spectrum. In Table III we write ''*w*'' (for weak), we may say that the intensity is about one order of magnitude lower than for the four main peaks.

Let us now analyze these results. The absence of peaks 142, 143, 145, 147, 149, 150 is consistent with the result obtained for copper since these masses correspond to heteroisotopes. We may notice that the effect is important for some masses; for example, the 142 heteroisotope peak belongs to the high intensity group for the pure Ge LMIS and is

TABLE III. Measured currents for the various Ge_2^+ isotopes (arbitrary units) in the case of a pure germanium LMIS (first line) and a $Au_{0.73}Ge_{0.27}$ alloy LMIS (third line); *w* means weak (the intensity is about one order of magnitude lower than for the four main peaks). The absolute values of the first line cannot be compared to those of the third line because the tips are different. The second and fourth lines are the first and third line values normalized by dividing by the lightest isotope value. The fifth, sixth, and seventh lines give, respectively: the normalized natural abundances, the normalized natural abundances when only homoisotopes are considered, the normalized natural abundances when homoisotopes plus 18% of the heteroisotopes with $\Delta m \leqslant 2$ (see text) are considered. This proportion of heteroisotopes is fixed so that the calculated $^{146}Ge_2^+$ intensity agrees with the experimental one.

	140	142	143	144	145	146	147	148	149	150	152
Ge_2^+	70.70	70.72	70.73	72.72 +70.74	72.73	73.73 +70.76 +72.74	73.74	74.74 +72.76	73.76	74.76	76.76
Germanium	1.12×10^5	1.5×10^5	1.12×10^5	2.24×10.5	1.19×10^5	2.37×10^5	1.19×10^5	2×10^5	1.06×10^5	1.26×10^5	0.24×10^5
Norm.	1	1.34	1	2	1.06	2.11	1.06	1.78	0.94	1.12	0.21
Alloy	2.37×10^5	*w*	*w*	2.5×10^5	*w*	2.5×10^5	*w*	2.5×10^5	*w*	*w*	*w*
Norm.	1	*w*	*w*	1.06	*w*	1.06	*w*	1.06	*w*	*w*	*w*
Stat.	1	2.67	0.76	5.36	1	5.8	1.33	4.18	0.28	1.33	0.14
Homoisotopes	1	0	0	1.79	0	0.14	0	3.16	0	0	0.14
Homoisotopes + 18% others	1	0.47	0	1.79	0.16	1	0.24	3.16	0	0.24	0.14

weak for the alloy. However it remains an unexplained feature. If the intensity of peak 146 were only due to the homoisotopic specy, it should be present with a weak normalized intensity (0.14), while the experiment gives a value close to one. For explaining this point we may say that a part of the 72–74 heteroisotope contributes to the 146 peak. Then it is easy to see that 18% of this heteroisotope is necessary for adjusting the relative intensity to one. In the previous estimation we have only added a contribution from the 72–74 isotope and not from the 70–76 isotope. This point will be justified later in the discussion where we show that the disappearance of an heteroisotope is more likely for large mass difference Δm between its atomic components. Following this last remark we give in the lowest row of Table III the normalized abundances obtained by adding a contribution of 18% heteroisotopes with $\Delta m \leqslant 2$. We see that the only calculated values larger or equal to one correspond to the four observed peaks. In conclusion we may say that for Ge_2^+ the emission from a $\mathrm{Au}_{0.73}\mathrm{Ge}_{0.27}$ LMIS is characterized by a strong reduction of the heteroisotopes.

Let us give some precisions concerning our experiments and the data presented in Tables I, II, and III. Our total currents are (for all the experiments) in the range $I = 3 \pm 1$ μA. This current includes all the positively charged species which are emitted with kinetic energies ranging from 0 to about 250 eV. A selection among these ions in a much smaller energy interval of about 3 eV is made by using an electrostatic analyzer which acts before the magnetic mass-spectrum analyzer. This is the reason why, in our experiments, the peaks are well resolved. The previous 3 eV kinetic energy interval is centered on an energy obtained experimentally after optimizing the most intense monoatomic specy current. Our knowledge of the energy distribution of the monoatomic species[13] allows us to say that this energy is not too far from the zero energy (1 to 10 eV) depending on the element.

Each result given in the tables has been obtained from one spectrum representative of the general behavior obtained in other experiments. We give an approximate 30% relative error. A better procedure would have been to make an averaging on various spectra, however, one may consider that, due both to the instabilities of the LMIS currents and the large magnitude of the isotopic observed effect (mainly for Cu_2^+), our results are significant. This is a first study and improvements in this point will be brought in a future work.

III. POSSIBLE INTERPRETATION

The previous effect may be interpreted by two kinds of models. We will first examine a possible segregation at the surface of the emitting zone and will then discuss the emission process.

Important segregation effects have been observed in alloy LMIS experiments, for example in the GaIn study.[14] In this last case the Ga^+ angular distribution is strongly directed along the tips axis while the In^+ angular distribution presents a maximum for an angle of about 15° with the axis. This phenomenon is explained by a segregation effect[14] with migration of Ga towards the tip summit. The energy distributions of Ga^+ and In^+ are also different from each other and exhibit particular features which can be related to the previous segregation effect.

In our experiment a complete segregation at the alloy surface between the various M isotopes ($M = \mathrm{Cu,Ge}$) would explain the observed phenomenon since the formation of M_2^+ heteroisotopes would be forbidden. But here the elements are chemically identical and the masses close to each others, as a consequence the segregation effect is certainly less important than in the InGa case. Moreover we have measured the energy distribution of $^{63}\mathrm{Cu}^+$ and $^{65}\mathrm{Cu}^+$ emitted by the $\mathrm{Au}_{0.5}\mathrm{Cu}_{0.5}$ LMIS and have not observed any significant difference between the two curves (these results will be published in a forthcoming paper) while noticeable differences appeared in the GaIn LMIS study.[14] Then, even if a segregation effect appears which will reduce the probability of formation of heteroisotope dimers, it is doubtful that this only phenomenon can explain the observed effect.

Then we are led to abandon this first track of interpretation and come to examine the emission process. Let us first recall the Kingham post-ionization mechanism[15] which describes the emission of atomic multiply charged ions.[16] In this model one considers a positive singly charged ion, M^+, which has been extracted by field emission from the liquid metal or alloy. At time $t = 0$ this ion is supposed to be close to the surface $(z = 0)$. Under the action of the electric field it leaves the surface in the direction of decreasing potentials (for the global positive charge). Simultaneously the potential energy of the outer electron (negative charge) of M^+ increases and equals eEz when M^+ reaches abcissa z. When eEz is equal to the difference, $I_2 - \phi$, between the energy of second ionization and the liquid work function (which happens at distance z_c given by $eEz_c = I_2 - \phi$), the outer electron may tunnel from M^+ to the free bulk levels, giving then a doubly M^{2+} ion. If we take $E \sim 2$ V/Å (Ref. 15) and $I - \phi \sim 10$ eV we obtain typically $z_c \sim 5$ Å.

Let us now examine how the previous ideas can be adapted to M_2^+ ions. As before we will admit that the M_2^+ ions have been extracted by field emission and will suppose that at time $t = 0$ it is perpendicular to the surface with the light atom at abcissa $z = 0$ and the heavy one at $z = d$. In the same way as in the Kingham model the electric field has two actions. It puts into motion the positive M_2^+ ion whose potential energy decreases with z (we call z the distance of the M_2^+ center from the surface) and it simultaneously promotes the potential energy of the outer electron by an energy eEz. In a precise description we should add a third kind of action, i.e., the polarization of the external electron. In this simple scheme we will neglect this effect which is also neglected in the Kingham atomic theory.[15] The polarization effect being neglected means that each of the two nuclei brings an equal average charge of $+e/2$. This allows us to study their motions. For calculating the spatial contraction Δz between the two nuclei we will assimilate the M_2^+ dimer to an oscillator with frequency ω, then a classical calculation gives

$$\Delta z = \Delta z(\omega = 0)\,\frac{2}{\omega^2 t^2}(1 - \cos\omega t) \tag{1}$$

with

$$\Delta z(\omega=0)=z\frac{\Delta m}{m} \tag{2}$$

and

$$z\cong\frac{eE}{2m}\frac{t^2}{2}. \tag{3}$$

t is the time needed to reach distance z, m, and Δm are the average mass and the mass difference, respectively. The potential energy difference between the two nuclei is

$$\Delta U=eE\Delta z.$$

If we take $z\sim5$ Å and $E\sim2$ V/Å, as we did in the previous example, one obtains for $\omega\sim1.5\times10^{-13}\ \mathrm{s}^{-1}$ (this value will be justified below):

$$\Delta U=0.08\ \ \mathrm{eV}.$$

The previous calculation is made for $\Delta m=2$ and $m=64$ which is the case of Cu but the same order of magnitude is expected for Ge. Now let us discuss our ω value which corresponds to an energy of 75 cm^{-1}. This discussion will be made for Cu_2^+ where theoretical results are available. These calculations give 150 cm^{-1} for the Cu_2^+ ground state.[17] This value agrees with the results obtained in Refs. 18 and 19 for Ag_2^+ and Au_2^+. But, in the choice of ω, we have to include the fact that the M_2^+ species are certainly raised in excited electronic states which will lead to lower energies. For example, in the Cu_2 case it goes from 260 cm^{-1} for the ground state to 90 cm^{-1} for some excited states.[20] As calculations on Cu_2^+ excited states are lacking we have chosen an ω value which is half the ground-state value, by doing so we use a reduction factor similar to the previous Cu_2 case.

We will assume that the previous estimation can be extended to Ge_2^+ isotopes (with $\Delta m=2$). Of course only the knowledge of Ge_2^+ potential energy curves (which give ω) could validate the previous assumption.

A remark can also be made on the E value. We have used $E\sim2$ V/Å but larger values might also been introduced.[21] Then, as t decreases as $1/E^2$, the $(2/\omega^2t^2)(1-\cos\omega t)$ factor in formula (1) increases and ΔU values close to $\Delta U(\omega=0)=0.31$ eV can be reached. In a more precise calculation one should also include the various possible orientations of the dimers at time $t=0$. Nevertheless, we see that an excitation energy of the order of one tenth of eV which may be transmitted to the outer electron only appears in the heteroisotopic M_2^+.

By taking into account the eEz electrostatic energy and the ΔU excitation energy we can write that, for an heteroisotope, a second ionization will be possible at the distance z_c' given by $eE\,z_c'=I_2'-\Delta U-\phi$ where I_2' is the energy needed for ejecting the outer M_2^+ electron. Let us notice that in the case of Cu_2^+ this ionization will break the dimer, since $N=2$ is below the critical size;[4] for Ge_2^+ it will lead to Ge_2^{2+}. The previous model would allow one to understand the experimental observations. On the one hand, the ΔU term shows that the heteroisotopic species may be excited with respect to the homoisotopic ones. On the other hand, when going from the pure M LMIS to the alloy, free bulk levels are available at lower energies. Indeed, in the AuCu case, we know that $\phi_{\mathrm{Cu}}=4.65$ eV and $\phi_{\mathrm{Au}}=5.1$ eV and therefore ϕ_{CuAu} is certainly larger than ϕ_{Cu}. In the case of AuGe (where the work functions are similar for Au and Ge) the presence of Au introduces levels at energies which fall into the gap and were forbidden for Ge. Therefore the disappearance of M_2^+ heteroisotopes in AuM LMIS emission would be due to the conjunction of the two previous effects: presence of a ΔU term specific to heteroisotopes and lower energy levels available in alloy LMIS. We also understand now why in the first section we only consider the possible existence of Ge_2^+ heteroisotopes with an atomic mass difference $\Delta m\leqslant2$. Indeed, as ΔU increases with Δm the heteroisotopes with $\Delta m>2$ have a large excitation energy and according to the previous model one may think that they disappear.

To conclude one may say that many possible experiments may be proposed for controlling the present interpretation. For example, the emission of Cu_2^+ from a AgCu alloy should not lead to the same anomaly as AuCu because $\phi_{\mathrm{Ag}}=4.62$ eV is of the order of ϕ_{Cu}. Moreover the Sb_2^+ ions would provide an interesting system because there are only two atomic isotopes with almost equal relative abundances (^{121}Sb 57.25; ^{123}Sb 42.75). Let us notice that the alloy clusters $\mathrm{Cu}_n\mathrm{Sb}_m$ produced by a gas aggregation source have already been studied.[22]

It is also worth noting that in a previous work by Machalett and Mühle[5] on a $\mathrm{Cu}_{63.5}\mathrm{Ge}_{36.5}$ LMIS the Cu_2^+ ions have already been observed. As the purpose in this paper was not to study possible isotopic anomalies, nothing was said about this point, however according to Fig. 1 of this article[5] it seems that only two isotopes appear. This result might also been explained by the previous model.

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