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ENRICHMENT OF THE SUPERHEAVY ELEMENT ROENTGENIUM (Rg) IN NATURAL Au

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Based on the observation of the long-lived isotopes of roentgenium, ^{261}Rg and ^{265}Rg ($Z = 111$, $t_{1/2} \geq 10^8$ y) in natural Au, an experiment was performed to enrich Rg in 99.999% Au. 16 mg of Au were heated in vacuum for two weeks at a temperature of 1127°C (63°C above the melting point of Au). The content of ^{197}Au and ^{261}Rg in the residue was studied with high resolution inductively coupled plasma-sector field mass spectrometry (ICP-SFMS). The residue of Au was 3×10^{-6} of its original quantity. The recovery of Rg was a few percent. The abundance of Rg compared to Au in the enriched solution was about 2×10^{-6}, which is a three to four orders of magnitude enrichment. It is concluded that the evaporation rate of Rg from an Au matrix in vacuum at 63°C above the Au melting point is lower than that of Au. This experiment reinforces our first observation of Rg in a terrestrial material. As before it is concluded that a long-lived isomeric state exists in ^{261}Rg and that it probably belongs to a new class of isomeric states, namely high spin (K-type) super- or hyperdeformed isomeric states.

Keywords: Atomic mass measurements; long-lived isomeric states; superheavy elements; superdeformation; hyperdeformation; ^{261}Rg.

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1. Introduction

In recent years long-lived isomeric states have been reported in several isotopes found in natural materials.[1–3] They, for instance, were seen in the neutron deficient ^{211}Th, ^{213}Th, ^{217}Th and ^{218}Th isotopes, with estimated half-lives of $\geq 1 \times 10^8$ y, which is 16 to 22 orders of magnitude longer than the known half-lives of their corresponding g.s.[1,4] They were also observed in the superheavy element region.[2,3]

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Isotopes with atomic mass numbers 261 and 265 have been reported in natural Au (Ref. 2) and interpreted as long-lived isomeric states in ^{261}Rg and ^{265}Rg, since Rg ($Z = 111$) is a chemical homolog of Au.[5] In the superactinides, a nucleus with atomic mass number 292 has been found in purified Th and interpreted as most probably a nucleus with atomic number 122, because element 122 is predicted to be eka-Th.[5,6] Since all these nuclei were observed in natural materials it was deduced that the lower limit on their half-lives should be about 1×10^8 y, or otherwise they would have decayed away. The predicted half-lives for ^{261}Rg, ^{265}Rg and ^{292}122 in their normally deformed g.s. are in the region of 10^{-6} to 10^{-8} s.[7] Therefore it was concluded that, like in the neutron-deficient Th isotopes, these nuclei are also in long-lived isomeric states. It was hypothesized that they may belong to a new class of high spin (K-type) superdeformed (SD) or hyperdeformed (HD) isomeric states. Such isomeric states have been seen in ^{195}Hg (Ref. 8), in ^{210}Fr (Refs. 9 and 10) and in heavy actinide nuclei like ^{236}Am, ^{236}Bk (Ref. 11), ^{247}Es and ^{252}No (Ref. 12). Their character as high spin SD and HD isomeric states has been proven by observation of abnormal α-particle groups in coincidence with γ-rays of SD bands.[8,9]

In the experiments of Refs. 2 and 3 it was assumed that the chemical procedures used by the purveyors of separated Au and Th were not so specific as to separate the heavy homologs Rg and eka-Th from Au and Th, respectively. The purpose of the present experiment was to try to concentrate Rg in Au. If the evaporation rate of Rg is lower than that of Au from a melt, it may be possible to enrich Rg in Au by keeping the Au in vacuum a little over its melting point. One may thus preferentially evaporate Au relative to Rg. The evaporation rate of Au compared to Rg depends first on the dissociation energy of Au_2 dimer (or Au_n) compared to RgAu (or $RgAu_{n-1}$), and secondly on the probability that the free atoms will sublime from the melt to the vacuum. It is reasonable to assume that because of the different masses, Au will sublime easier than Rg. As for the first step there are some predictions[13] that the dissociation energy of RgAu is lower than that of Au_2, about 1.5 eV as compared to 2.2 eV, respectively.

As before[1–3] accurate mass measurements, using ICP-SFMS, have been employed on mass 261 to identify ^{261}Rg. The mass M_A of an atom is equal to:

$$M_A = ZM_H + NM_n - \mathrm{BE}\,, \tag{1}$$

where Z and N are the number of protons and neutrons in the atomic nucleus, M_H and M_n are the masses of the hydrogen atom and of the neutron, respectively, and BE is the binding energy of the atom. The binding energy per nucleon (BE/u) as a function of A for stable nuclei has a maximum at about $A = 60$ and then drops monotonically towards higher A.[14] Therefore, the mass of a heavy atom is higher than and separated from the mass of any molecule (except for multi-H, -Li, -Be and -B molecules) with the same mass number.

This is seen in Fig. 1, where the systematic behavior of the masses[15] of various $M = 261$ species, from the quasi-symmetric combination ^{133}Cs^{128}Te to Au-, Bi-, Th- and U-based molecules to the predicted[16–18] mass of the ^{261}Rg nucleus

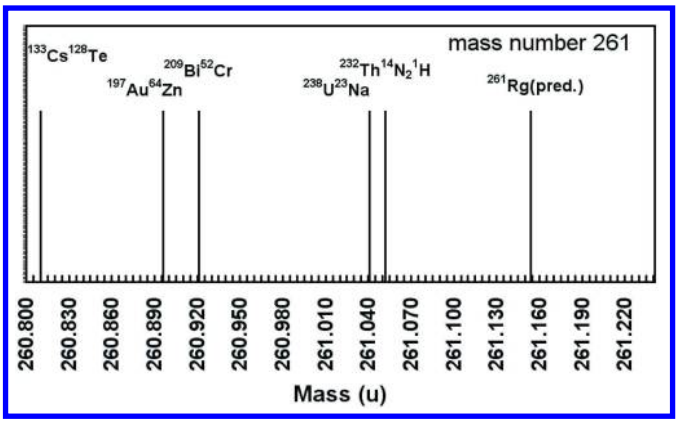

Fig. 1. Representation of the systematic behavior of the masses of various $M = 261$ species, ranging from $^{133}Cs^{128}Te$ to Au- Bi-, Th- and U-based molecules,[15] to the predicted[16–18] mass of ^{261}Rg.

is displayed. The mass of the very neutron-rich ^{261}Au nucleus is predicted to be 261.337 u (Ref. 16) or 261.324 u (Ref. 18), values well above the expected mass of the ^{261}Rg nucleus, which is 261.154 u (Refs. 16–18). (The calculations[16–18] of the ^{261}Rg mass agree to within 0.002 u.) Thus, as was demonstrated before,[2,3] accurate mass measurements are an effective tool for detecting naturally-occurring superheavy elements.

In the present experiment, an Au solution enriched in Rg has been produced. Accurate mass measurements in the region of mass 261 were performed using ICP-SFMS with a resolution $m/\Delta m = 4000$. A peak that fits with the predicted mass of ^{261}Rg and does not fit with any known molecule has been observed. The recovery of Rg was a few percent. An enrichment factor of three to four orders of magnitude has been obtained. It is deduced that under our experimental conditions the evaporation rate of Rg is lower than that of Au.

2. Experimental Procedure

16 mg of 99.999% Au metal, supplied by Leico Industries, were held in a quartz tube in vacuum for two weeks at a temperature of 1127°C (63°C above the melting point of Au). The heating was stopped when the residue could no longer be seen with a magnifying glass. The minute residue was dissolved overnight in aqua regia at 60°C. After evaporating almost to dryness, 3 M HNO_3 was added and diluted to obtain a final volume of 20 ml at 0.7 M HNO_3. This solution was studied with the ICP-SFMS.

The accurate mass measurements were similar to those described before.[1–3] The ICP-SFMS was a Finnigan Element2 (Thermo-Electron, Bremen, Germany). In this instrument a solution of the material to be studied is introduced into a high temperature (6000–8000 K) plasma source. At these temperatures predominantly atomic species are present. Molecular ions are formed after the source, mainly by interac-

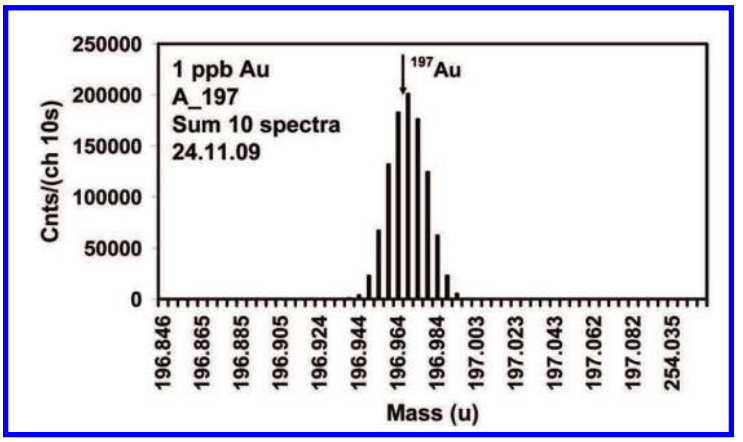

Fig. 2. Measurements of mass 197 obtained with 1 ppb Au solution. The sum of ten measurements is displayed. Total measuring time: 700 s. Observed mass position: 196.969 u. Known mass of ^{197}Au (indicated by an arrow) is 196.967 u.[15]

tion with oxygen and hydrogen ions from the solution. The predefined resolution mode, $m/\Delta m = 4000$ (10% valley definition), was used throughout the experiments to separate atomic ions from molecules with the same mass number. The sensitivity-enhanced setup of the instrument was similar to that described in Ref. 19. In the present experiment the sample uptake rate was 50 μl min^{-1} and the sensitivity for ^{197}Au in this resolution mode was 2×10^7 counts s^{-1}mg^{-1}l^{-1}. Methane gas was added to the plasma to decrease the formation of molecular ions.[20] Oxide and hydride formation (monitored as UO^+/U^+ and UH^+/U^+ intensity ratios) were approximately 0.04 and 1×10^{-5}, respectively. Mass calibration was performed using the $^{115}In^+$, $^{232}Th^+$, $^{235}U^+$, $^{238}U^+$ and $^{238}U^{16}O^+$ peaks. The extrapolation from mass 254 ($^{238}U^{16}O$) to mass 261 covers only 5% of the 115–254 mass region over which the calibration was performed. The maximum deviation of the $^{238}U^{16}O$ peak (mass 254) measured after every spectrum across the ninety spectra taken for mass 261 was 0.012 u. A calibration correction of 0.037 u was deduced from these measurements (see below) and applied to the data.

Complete elemental screening was performed on the enriched Rg solution to assess the impurity levels. The amount of certain trace elements with relatively high concentrations, expressed as ppb (g/g) of the solution are as follows:

Au 4.1, Ca 140, Cl 15600, K 250, Na 360, P 150, S 780, Si 40, Th 0.001, U 0.04.

These concentrations are correct to within a factor of two. After these impurity determinations, the solution was spiked to 1 ppb of U. These levels of contamination are higher than those specified in Ref. 2 where pure original Au solution was used. (The corresponding values there for Na and S were in the region of a few ppb.) A synthetic solution which contains the above-mentioned impurities with their measured concentrations, spiked to 1 ppb of U, was prepared and used for comparison in the experiments.

After a two-hour warm-up, the machine was still unstable. Therefore the measurements were started after nine hours of stabilization. A range of 0.45 u, divided into 70 channels, was scanned in each spectrum. The scanning was performed by changing the acceleration voltage while keeping the magnetic field constant. The mass 261 was analyzed with an integration time per channel of 1 s and run 90 times.

3. Results and Discussion

Figure 2 shows the sum spectrum of ten measurements of mass 197 (^{197}Au) taken with a 1 ppb (g/g) Au solution. The FWHM of the peak is 0.038 u.

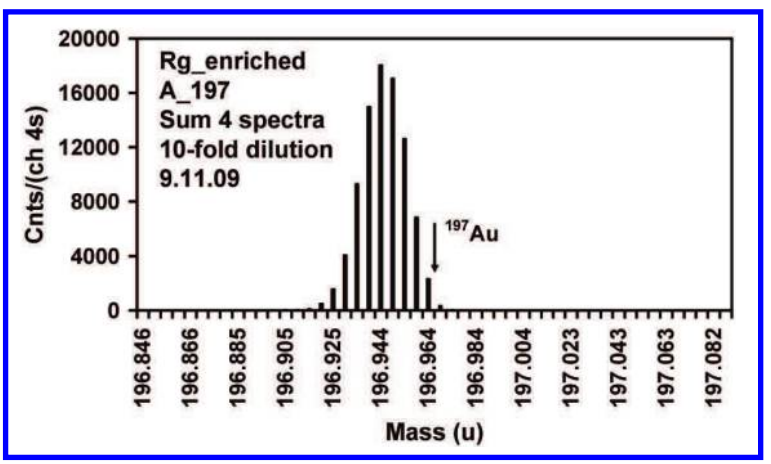

Fig. 3. Measurements of mass 197 obtained with a ten-fold diluted sample of the enriched Rg solution. The sum of four measurements is displayed. Total measuring time: 280 s. Observed mass position: 196.945 u. Known mass of ^{197}Au (indicated by an arrow) is 196.967 u.[15]

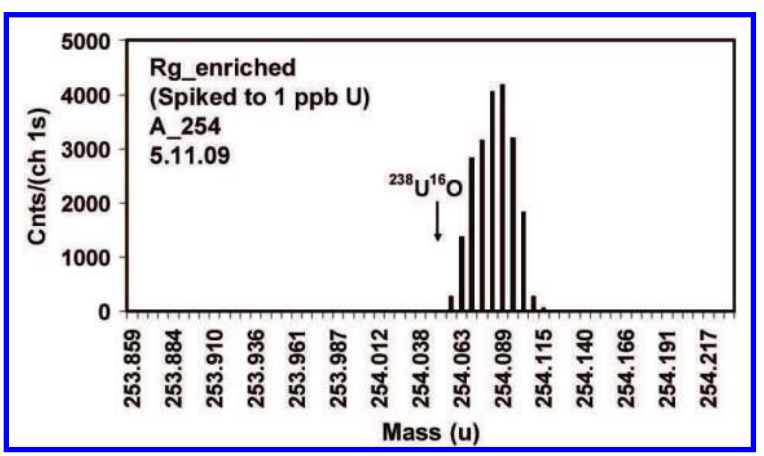

Fig. 4. Measurement of mass 254 obtained with the enriched Rg solution which was spiked to 1 ppb U (see text). Total measuring time: 70 s. Observed mass position: 254.084 u. It is shifted from the known mass of ^{238}U^{16}O of 254.046 u (Ref. 15) (indicated by an arrow) by 0.038 u.

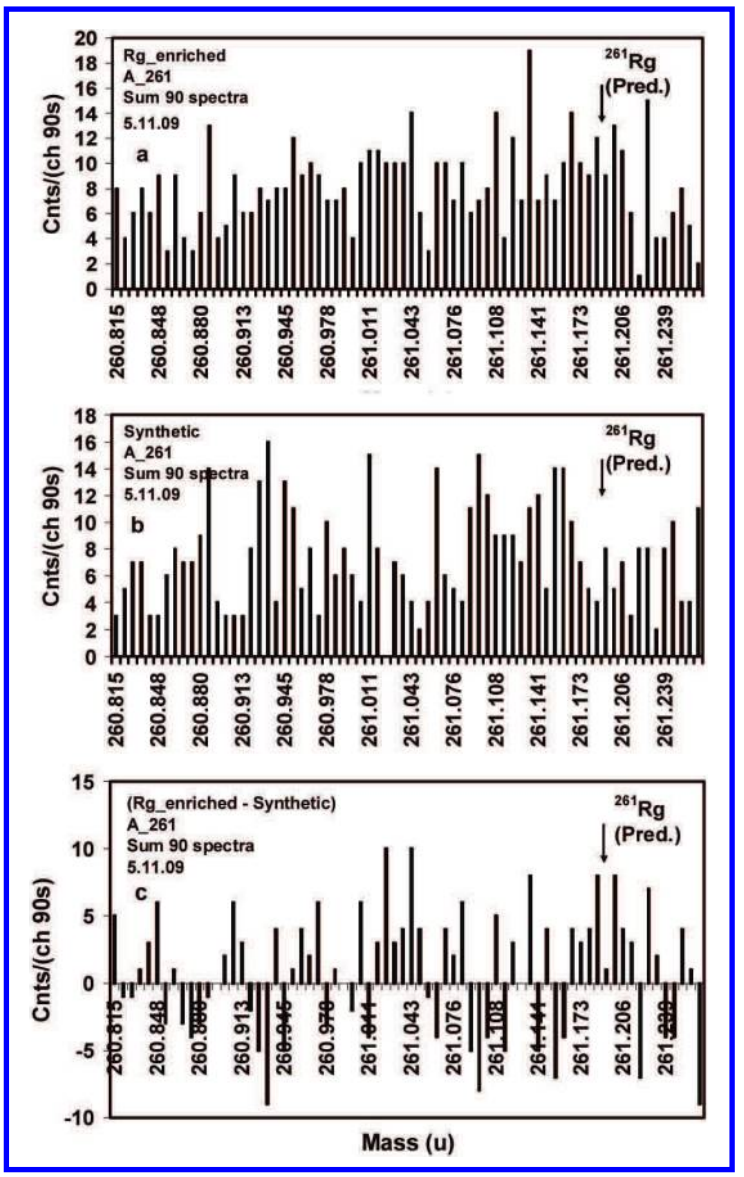

Fig. 5. Measurements of mass 261 obtained with the enriched Rg solution (a), and with the synthetic solution (b). Spectrum (c) represents the subtraction of spectrum (b) from spectrum (a). The sum of 90 spectra is displayed in each case. Total measuring time: 6300 s in spectra (a) and (b). The arrows indicate the predicted position of ^{261}Rg (m = 261.154 u)[16–18] shifted by a calibration correction of 0.037 u (see text).

Figure 3 shows the sum of four measurements of mass 197, taken with a ten-fold diluted sample of the enriched Rg solution. The peak of ^{197}Au is shifted from its known value[15] by −0.022 u. By a comparison of Figs. 2 and 3 it is concluded that the Au concentration in the enriched Rg solution is 2.2 ppb (g/g). It is therefore

deduced that the residue of Au in this 20 ml solution is 44 ng which is about 3×10^{-6} of its initial value of 16 mg.

Figure 4 shows the results obtained on mass 254 measured with the enriched Rg solution which was spiked to 1 ppb U. It was taken before performing the measurements on mass 261. The peak of $^{238}U^{16}O$ is seen and it is shifted from the known value[15] by 0.038 u. A similar spectrum taken after the mass region 261 measurements were finished gave a shift of 0.036 u. An average correction of 0.037 u was applied to the data.

Figure 5 shows the sum of 90 spectra obtained on mass 261 with the enriched Rg solution (a) and with the synthetic solution (b). Figure 5(c) presents the subtraction of spectrum (b) from spectrum (a). A peak of 37 ± 13 counts is seen in Fig. 5(c) at the predicted position of ^{261}Rg (Refs. 16–18). The error estimate was calculated according to the formula $\sigma = (N_{\text{total}} + N_{\text{back}})^{1/2}$ (Ref. 21) where N_{total} is the total

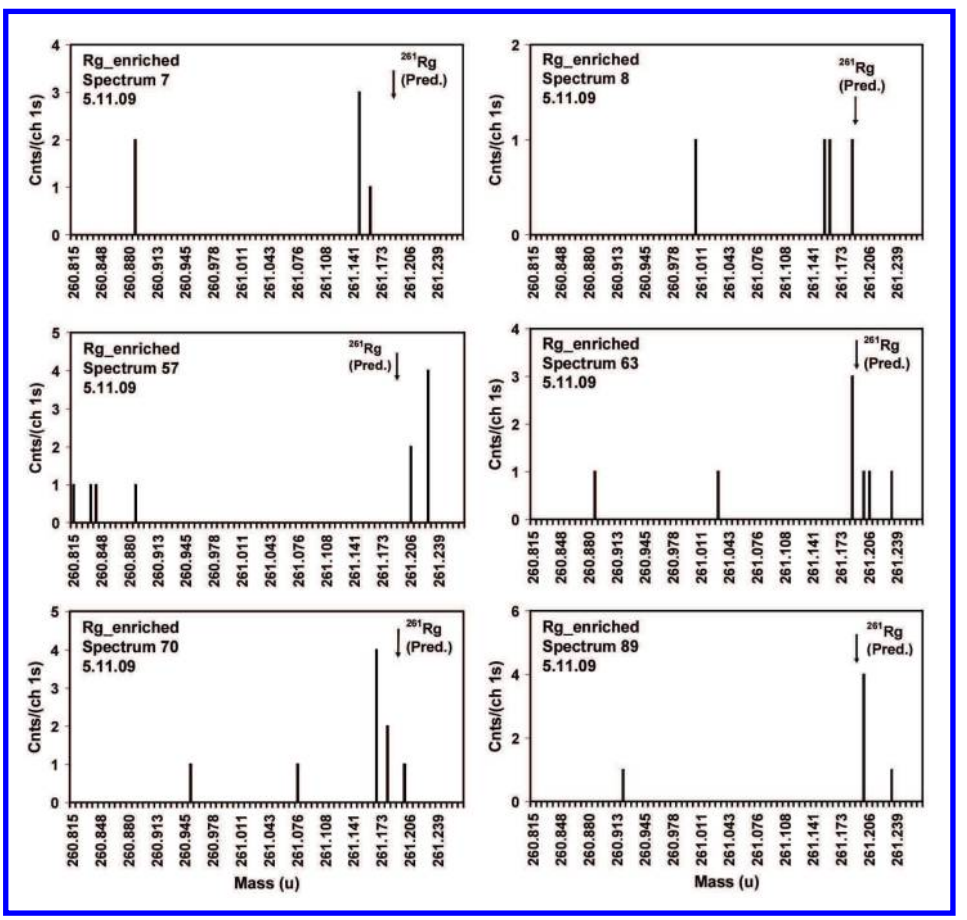

Fig. 6. Six individual spectra at the mass region 261 obtained with the enriched Rg solution are shown. Total measuring time of each spectrum was 70 s. The arrows indicate the predicted position of ^{261}Rg ($m = 261.154$ u)[16–18] shifted by a calibration correction of 0.037 u (see text).

number of counts in the Rg region taken from Fig. 5(a) and $N_{\rm back}$ is the number of background counts taken from Fig. 5(b).

The 90 measured spectra are independent of one another. At low abundance level of about 10^{-15} of the solution (see below) it is possible that, due to some instability in the plasma ion source, in some spectra the peak of atomic ions will be more pronounced than that of molecular ions and vice-versa in other spectra. Such behavior has been seen by us for instance in a study of the known molecule $^{232}Th^{40}Ar^{16}O$ at 0.1 ppm of Th, where in one spectrum 12 counts were seen and in the spectrum measured immediately afterward, one count was observed. In the spectrum of Fig. 5(a) 130 counts are seen in the region of interest (ROI) of ± 0.044 u around the predicted position of ^{261}Rg. In the region out of interest (OROI) from 260.815 to 261.147 u (3.8 times larger than the ROI) there are 420 counts. If the group of events around the predicted position of ^{261}Rg is due to background, then the ratio $N_{\rm OROI}/N_{\rm ROI} = 3.23 \pm 0.44$ should be about the same in each individual spectrum. In 26 spectra events were seen at the predicted mass of ^{261}Rg. In 11 spectra it was found that this ratio is quite different from 3.23, between 0.2 and 1.4 with an average value of 0.6. These spectra are dominated by counts around the predicted position of ^{261}Rg. The data are as follows: (Spectrum number; $N_{\rm ROI}$; $N_{\rm OROI}$; $N_{\rm OROI}/N_{\rm ROI}$): (1; 2; 1; 0.5), (7; 4; 2; 0.5), (8; 3; 1; 0.3), (27; 2; 1; 0.5), (57; 6; 4; 0.7), (63; 6; 2; 0.3), (69; 4; 3; 0.8), (70; 7; 2; 0.3), (79; 5; 7; 1.4), (84; 4; 4; 1.0), (89; 5; 1; 0.2). These results are displayed in Figs. 6 and 7.

In Fig. 6, an example of six out of the 11 mentioned spectra are seen. In these as well as in most of the 11 spectra, more events are seen in the high mass region, around the predicted ^{261}Rg position, than in the rest of the measured region.

In Fig. 7 the sum of the 11 spectra is shown. A pronounced peak of 48 counts is seen at mass 261.144 ± 0.020 u (taking into account the calibration shift). The total

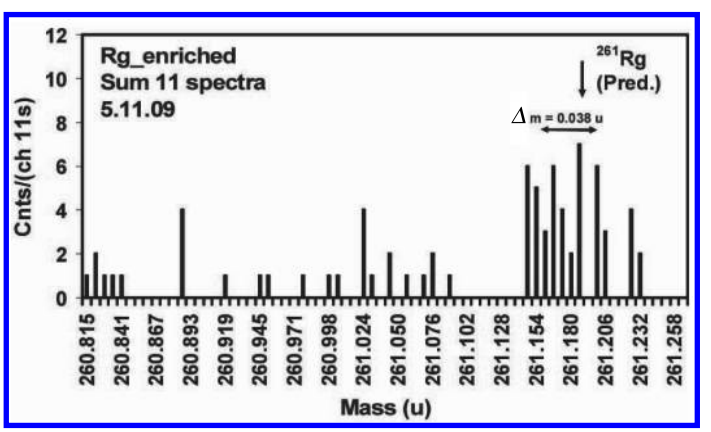

Fig. 7. Measurements of mass 261 obtained with the enriched Rg solution. The sum of 11 measurements is displayed. Total measuring time: 770 s. Observed mass position, corrected by a calibration shift of 0.037 u, is 261.144 ± 0.020 u. Predicted mass[16–18] for ^{261}Rg (indicated by an arrow) is 261.154 u. $\Delta m = 0.038$ u denotes the FWHM as obtained from Fig. 2.

number of events OROI is 28. The ratio $N_{\mathrm{OROI}}/N_{\mathrm{ROI}} = 0.58 \pm 0.19$ as compared to 3.23 ± 0.44 observed in Fig. 5(a). It is therefore concluded that the peak in Fig. 7 is not due to background. The observed mass of this peak fits, within 0.010 u, with the predicted mass[16–18] of ^{261}Rg of 161.154 u. It is larger than the mass of any molecule with $M = 261$ (except for multi-H, -Li, -Be and -B molecules) as seen in Fig. 1. By a comparison with Fig. 3 the average intensity of this peak in the 90 spectra, compared to ^{197}Au is about 2×10^{-6} (4×10^{-15} of the solution). It is about a factor of ten larger in the 11 spectra mentioned above, about 4×10^{-14} of the solution. Thus, an enrichment of three to four orders of magnitude, compared to the earlier determined abundance of $(1-10) \times 10^{-10}$ (Ref. 2), has been achieved in this experiment. The recovery of Rg from the initial Au is estimated to be a few percent. The high enrichment factor shows that the evaporation rate of Rg in a matrix of Au is lower than that of Au.

4. Summary

In summary, the present results strengthen the first observation[2] of the superheavy element Rg ($Z = 111$) in nature. As was argued in Ref. 2, if its terrestrial concentration about 4.5×10^9 y ago was similar to that of Au, then the half-life of the observed ^{261}Rg nucleus is $\geq 10^8$ y. Since the half-life of the normally deformed g.s. of ^{261}Rg (Ref. 7) is predicted to be about 1 μs, it was concluded[2] that the observed nucleus is in an isomeric state, probably unrelated to high-spin states near closed shells, fission isomers or K-isomers at normal deformations. It is therefore hypothesized[2] that it belongs to a new class of high spin (K-type) isomeric states in the SD or HD minimum of the nuclear potential energy.[8–10,12] This work also shows that it is possible to enrich Rg in purified Au by evaporating the Au in a vacuum at about 63°C above its melting point.

5. Comment

Very recently a paper by Dellinger *et al.*[22] has appeared, where an upper limit of about 10^{-16} was determined for the existence of ^{261}Rg in various Au minerals, using AMS technique. Whatever the difficulties that can arise between using the complicated AMS system and the straightforward ICP-SFMS equipment, an important difference between our work and the work of Ref. 22 is that we used separated Au extracted from large amount of material, and they used raw minerals. We mention that it may not be surprising that the result obtained with tiny random samplings of inhomogeneous natural minerals, in the region of a few mg, as in Ref. 22, would contrast with the concentration found in our purified Au starting material with its assumed homogeneously distributed Rg.

We also would like to point out that the results of Dellinger *et al.* may not all be negative. We refer in particular to Fig. 4(b) in Ref. 22 on ^{296}Rg. This spectrum is clean, without pile-up. One sees in this spectrum a group of five events very close to the estimated position of ^{296}Rg. This peak appears at a residual energy of about

10.5 MeV, where according to the authors, its center should appear at 12.0 MeV. Such a difference of 1.5 MeV out of a predicted energy loss in the detector window of 12 MeV (about half of the initial energy of the ions of about 24 MeV) could arise from experimental and theoretical uncertainties. Besides window thickness and energy calibration of the AMS detector, there could be uncertainties in the energy loss and range when extrapolated to an unstudied heavy nucleus like Rg. In addition, the appreciable accumulated scatter of these ions in the detector window, due to their large energy loss, decreases the residual energy of the ions in the detector. In conclusion, a residual energy of 10.5 MeV instead of 12 MeV for ^{296}Rg, when the total energy loss in the window is about 12 MeV, could be within the uncertainties inherent in the experiments.

If ^{296}Rg has been observed in these experiments, then it is a very important result. With $Z = 111$ and $N = 185$ it would be in the center of the island of stability predicted for nuclei in their normal g.s. Since if found in natural materials, its half-life should be $\geq 10^8$ y. However, the predicted half-life for ^{296}Rg in its normal g.s. is 4.5×10^6 s.[7] A consistent interpretation is that, like in ^{211,213,217,218}Th (Ref. 1), ^{261,265}Rg (Ref. 2) and ^{292}eka-Th (Ref. 3), long-lived isomeric states exist in ^{296}Rg.

Acknowledgments

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References

1. A. Marinov, I. Rodushkin, Y. Kashiv, L. Halicz, I. Segal, A. Pape, R. V. Gentry, H. W. Miller, D. Kolb and R. Brandt, *Phys. Rev. C* **76** (2007) 021303(R).
2. A. Marinov, I. Rodushkin, A. Pape, Y. Kashiv, D. Kolb, R. Brandt, R. V. Gentry, H. W. Miller, L. Halicz and I. Segal, *Int. J. Mod. Phys. E* **18** (2009) 621.
3. A. Marinov, I. Rodushkin, D. Kolb, A. Pape, Y. Kashiv, R. Brandt, R. V. Gentry and H. W. Miller, *Int. J. Mod. Phys. E* **19** (2010) 131.
4. R. B. Firestone *et al.* (eds.), *Table of Isotopes* (John Wiley and Sons, New York, 1996).
5. G. T. Seaborg, *Annu. Rev. Nucl. Sci.* **18** (1968) 53.
6. E. Eliav, A. Landau, Y. Ishikawa and U. Kaldor, *J. Phys. B: Atom. Mol. Opt. Phys.* **35** (2002) 1693.
7. P. Möller, J. R. Nix and K.-L. Kratz, *Atom. Data Nucl. Data Tables* **66** (1997) 131.
8. A. Marinov, S. Gelberg and D. Kolb, *Int. J. Mod. Phys. E* **10** (2001) 185.
9. A. Marinov, S. Gelberg and D. Kolb, *Mod. Phys. Lett. A* **11** (1996) 861.
10. A. Marinov, S. Gelberg and D. Kolb, *Mod. Phys. Lett. A* **11** (1996) 949.
11. A. Marinov, S. Eshhar and D. Kolb, *Phys. Lett. B* **191** (1987) 36.
12. A. Marinov, S. Gelberg, D. Kolb and J. L. Weil, *Int. J. Mod. Phys. E* **10** (2001) 209.
13. W. Liu and C. van Wu, *J. Chem. Phys.* **110** (1999) 3730.
14. R. D. Evans, *The Atomic Nucleus* (McGraw-Hill, New York, 1955).
15. G. Audi, A. H. Wapstra and C. Thibault, *Nucl. Phys. A* **729** (2003) 337.

16. P. Möller, J. R. Nix, W. D. Myers and W. J. Swiatecki, *Atom. Data Nucl. Data Tables* **59** (1995) 185.
17. S. Liran, A. Marinov and N. Zeldes, *Phys. Rev. C* **62** (2000) 047301; arXiv:nucl-th/0102055.
18. H. Koura, T. Tachibana, M. Uno and M. Yamada, *Prog. Theor. Phys.* **113** (2005) 305.
19. I. Rodushkin, E. Engström, A. Stenberg and D. C. Baxter, *Anal. Bioanal. Chem.* **380** (2004) 247.
20. I. Rodushkin, P. Nordlund, E. Engström and D. C. Baxter, *J. Anal. Atom. Spectrom.* **20** (2005) 1250.
21. P. R. Bevington, *Data Reduction and Error Analysis for the Physical Sciences* (McGraw-Hill, New York, 1969).
22. F. Dellinger, W. Kutschera, O. Forstner, R. Golser, A. Priller, P. Steier, A. Wallner and G. Winkler, *Phys. Rev. C* **83** (2011) 015801.

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