

## <sup>197</sup>Au Mössbauer study of gold selenide, AuSe

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**Abstract.** The two crystallographic modifications of AuSe,  $\alpha$ -AuSe and  $\beta$ -AuSe, were studied by <sup>197</sup>Au Mössbauer spectroscopy. Despite the different crystal structures, the Mössbauer spectra of the two phases are nearly the same, and reveal the presence of two gold sites with Mössbauer parameters typical for Au<sup>I</sup> and Au<sup>III</sup>. The Mössbauer-Lamb factor of the Au<sup>I</sup> is less than half of that of the Au<sup>III</sup>. Calculations using the WIEN2k program reproduce the experimental results quite well and also yield the signs of the electric field gradients.

### 1. Introduction

In the gold-selenium system, only the intermetallic phase AuSe exists. Of this phase, however, two different crystallographic modifications are known,  $\alpha$ -AuSe and  $\beta$ -AuSe [1-3]. Both crystallize in the monoclinic space group C2/m, but with different lattice constants and with 4 ( $\beta$ -AuSe) or 8 ( $\alpha$ -AuSe) formula units in the unit cell.

In both modifications there are two different gold lattice sites: Half of the gold atoms occupy sites with a square-planar coordination to 4 nearest selenium neighbours at a distance of about 0.25 nm, while the other half occupies sites with a linear coordination to two nearest selenium neighbours at a distance of about 0.24 nm [3]. This prompted the idea that the gold on the former sites is Au<sup>III</sup>, while that on the latter ones is Au<sup>I</sup>. We have used Mössbauer spectroscopy with the 77 keV  $\gamma$  rays of <sup>197</sup>Au to confirm this assumption.

### 2. Experimental details

The Mössbauer experiments were performed at 4.2 K in a liquid He bath cryostat with sources of <sup>197</sup>Pt ( $T_{1/2} = 19$  h) produced by neutron irradiation of isotopically enriched <sup>196</sup>Pt metal in the Munich Research Reactor. The spectra were fitted with transmission integral lineshapes based on Lorentzian lines grouped into quadrupole doublets.

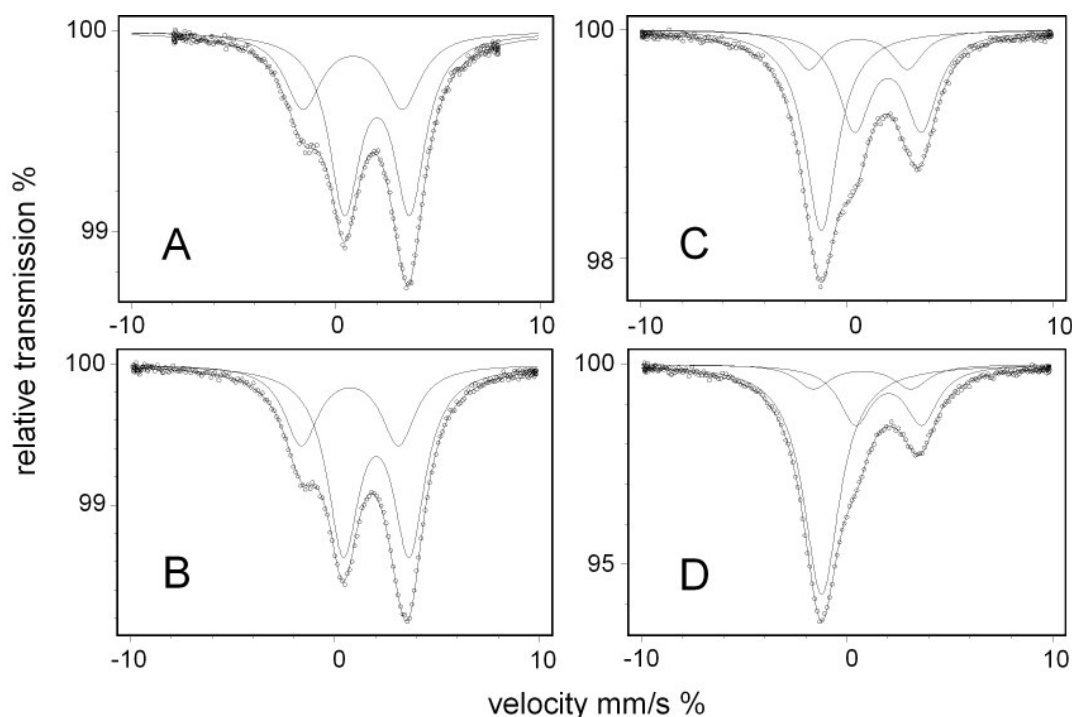
The gold selenides were prepared by reacting pellets of appropriate amounts of elemental gold and selenium powder in sealed quartz tubes. The materials thus obtained were analyzed by X-ray diffraction and 3 samples were selected for Mössbauer spectroscopy. A specimen with a composition of AuSe<sub>1.1</sub> kept for 120 days at 350°C yielded nearly pure  $\alpha$ -AuSe with only a minor  $\beta$ -phase impurity (Sample 1). By reacting a AuSe<sub>~1.3</sub> mixture at a temperature decreasing from 400 to 375°C within a day and subsequent annealing at 350°C for 120 days yielded a mixture of comparable amounts of  $\alpha$ -AuSe and  $\beta$ -AuSe (Sample 2). The best result of our efforts to prepare pure  $\beta$ -AuSe was obtained by keeping an AuSe mixture at 280°C for 18 days, which yielded almost pure  $\beta$ -AuSe with only a minor  $\alpha$ -phase impurity and some metallic gold (Sample 3).

### 3. Mössbauer Results and Discussion

The Mössbauer spectra of the 3 samples are shown in figure 1. Those of Samples 1 and 2 could be fitted with two overlapping symmetric quadrupole doublets. Since the right components of the two doublets nearly coincide, both a nested and a side-by-side arrangement of the doublets yield good fits. Figure 1 shows the latter fits, which yielded marginally better  $\chi^2$  values. The results of both ways of fitting the spectra are compiled in table 1. The spectrum of Sample 3 exhibits the two quadrupole doublets attributable to gold selenide and an additional component of metallic gold, whose isomer shift was fixed to the value of  $-1.22$  mm/s [4] in the least squares fits.

For Sample 1 ( $\alpha$ -AuSe) the doublet with the larger quadrupole splitting and smaller isomer shift can be attributed to  $\text{Au}^{\text{I}}$  and the other one to  $\text{Au}^{\text{III}}$ . On a plot of the quadrupole splittings versus the isomer shifts of  $\text{Au}^{\text{I}}$  and  $\text{Au}^{\text{III}}$  compounds [5], the values of both types of fit agree reasonably well with the notion that the gold on the two sites is  $\text{Au}^{\text{I}}$  and  $\text{Au}^{\text{III}}$ , respectively. One should keep in mind, however, that the electric quadrupole interactions are expected to be negative for  $\text{Au}^{\text{I}}$  and positive for  $\text{Au}^{\text{III}}$  [5], though the sign cannot be determined from the Mössbauer spectra of powder samples.

The fact that the spectrum of the mixture of comparable amounts of  $\alpha$ -AuSe and  $\beta$ -AuSe (Sample 2) is virtually identical to that of the nearly pure  $\alpha$ -phase (Sample 1) shows that the two phases yield nearly the same Mössbauer patterns. This is borne out by the Mössbauer parameters for Sample 3, which contains but very little of the  $\alpha$ -phase. We thus conclude that the hyperfine parameters for  $\alpha$ -AuSe and  $\beta$ -AuSe are the same within the accuracy of the Mössbauer measurements, and that two sets of parameters are possible because of the ambiguity in the fitting of the spectra.



**Figure 1.**  $^{197}\text{Au}$  Mössbauer spectra of gold selenides: (A) nearly pure  $\alpha$ -AuSe (Sample 1), (B) a roughly equal mixture of  $\alpha$ -AuSe and  $\beta$ -AuSe (Sample 2) and (C) nearly pure  $\beta$ -AuSe containing a minor amount of  $\alpha$ -AuSe and some metallic gold (Sample 3). A spectrum of Sample 2 with an additional absorber of metallic gold is also shown (D)

Although the amounts of gold on the two lattice sites of the gold selenides is the same, the  $\text{Au}^{\text{I}}$  component in the Mössbauer spectra exhibits less than half of the intensity of the  $\text{Au}^{\text{III}}$  component. This shows that the Lamb-Mössbauer factor  $f$  is much smaller for  $\text{Au}^{\text{I}}$  than for  $\text{Au}^{\text{III}}$ . For  $\alpha$ -AuSe

(Sample 1) one obtains  $f(\text{Au}^{\text{I}})/f(\text{Au}^{\text{III}}) = 0.40(3)$  from the intensities given in Table 1. The  $f$ -factor ratio for the  $\beta$ -phase is similar, but the experimental uncertainty is larger because of the presence of the Au metal impurity phase in Sample 3.

**Table 1.** Quadrupole splittings (QS), isomer shifts (IS) with respect to the Pt-metal source and relative spectral areas (A) of the two components attributable to  $\text{Au}^{\text{I}}$  and  $\text{Au}^{\text{III}}$  in gold selenides. Last digit errors are given in parentheses. The two sets of data given for each sample represent the two possible ways of fitting the spectra described in the text. When the relative intensities of the  $\text{Au}^{\text{I}}$  and  $\text{Au}^{\text{III}}$  components do not add up to 100%, the remainder represents the single line of metallic gold at  $-1.22$  mm/s with respect to the Pt metal source. D is the absorber thickness.

Sample	D (mg/cm <sup>2</sup> )	QS <sub>I</sub> (mm/s)	IS <sub>I</sub> (mm/s)	A <sub>I</sub> (%)	QS <sub>III</sub> (mm/s)	IS <sub>III</sub> (mm/s)	A <sub>III</sub> (%)
Sample 1	53	4.87(5)	0.82(3)	33.7(13)	3.19(3)	2.01(2)	66.3(13)
		5.57(7)	1.06(2)	27.5(9)	3.00(2)	1.89(2)	72.5(9)
Sample 2	82	4.76(5)	0.74(2)	31.4(8)	3.22(2)	2.03(2)	68.6(8)
		5.50(5)	1.09(2)	29.3(7)	2.94(3)	1.89(2)	70.7(7)
Sample 3	84	4.78(9)	0.55(6)	15.5(13)	3.24(3)	2.00(2)	40.3(13)
		5.89(7)	0.96(3)	12.2(7)	2.92(3)	1.82(2)	43.4(7)
2 + Au-metal	82 + 35	4.76*	0.74*	11.0(5)	3.22*	2.03*	25.2(5)
		5.89*	0.96*	8.3(3)	2.92*	1.82*	28.2(5)

\*Values fixed to those obtained for Sample 2 alone.

In order to obtain the  $f$ -factors for the two gold species relative to the  $f$ -factor of metallic gold ( $f = 0.189$  [7]), the absorber of Sample 2 (82 mg/cm<sup>2</sup>) was also measured together with an absorber of metallic gold (35 mg/cm<sup>2</sup>) [4]. From the mean intensity ratios observed in the resulting spectrum (figure 1 and table 1), and taking into account that Sample 2 has a nominal composition of  $\text{AuSe}_{1.3}$ , one obtains  $f(\text{Au}^{\text{I}})/f(\text{Au}_{\text{Metal}}) = 0.20(2)$  and  $f(\text{Au}^{\text{III}})/f(\text{Au}_{\text{Metal}}) = 0.55(2)$ . The small value of the  $f$ -factor for the  $\text{Au}^{\text{I}}$  species can be attributed to the large vibrational amplitudes of the gold perpendicular to the direction of the Se-Au-Se linear bonds. A similar situation has been observed for other  $\text{Au}^{\text{I}}$  compounds (e. g. [6, 8]).

#### 4. Calculations of the hyperfine parameters of $\alpha$ -AuSe and $\beta$ -AuSe

For comparison with the experimental results, the electric field gradients and electron densities at the Au nuclei in the gold selenides were calculated using the WIEN2k computer code [10, 11]. The Au 6s and 5d atomic states and the Se 4p states, which lie less than 1 Ry below the Fermi level, were treated as true valence states characterized by forming the (APW + lo) basis set. The Au 5p and Se 4s and Se 3d atomic states with binding energies of several Ry were described as local orbitals plus APW + lo wave functions. The atomic states with higher binding energies were considered as core states. About 100 APW + lo per atom in the unit cell and a k-mesh with 260–300 k-points in the irreducible mesh of the first Brillouin zone were used. The Fermi level was determined by the modified tetrahedron method [12] and the GGA parameterization [13] was used to calculate the exchange correlation energy. Muffin-tin radii of 2.50 a.u. and 2.16 a.u. were used for Au and Se, respectively. The optimization of the atomic positions was achieved via the PORT minimization facility of the WIEN2k program.

Values of the electron densities at the gold nuclei in a number of intermetallic gold compounds have previously [14] been obtained by calculations with the WIEN97 program, the predecessor of WIEN2k. These calculations were now repeated with the WIEN2k code. The results confirm the  $\Delta\langle r^2 \rangle$  given in [14] and were used together with the electron densities calculated for the AuSe phases to obtain the theoretical isomer shift values given in table 2. The isomer shift values for  $\text{Au}^{\text{III}}$  agree well with the experimental data, while those for  $\text{Au}^{\text{I}}$  are somewhat too small.

The  $V_{zz}$  value for the  $Au^I$  site is large and negative, as is expected for  $Au^I$  [4, 5], the  $Au^{III}$  value is smaller and positive (table 2). The EFG values decrease but slightly when the atomic positions are allowed to vary. The asymmetry parameter  $\eta$  is nearly zero for  $Au^I$  and small for  $Au^{III}$ . The conversion of the EFG data into electric quadrupole splittings is subject to the uncertainty in the value of the nuclear quadrupole moment of the ground state of  $^{197}Au$  [15]. We have used the value of  $Q = 0.56$  barn [16] to obtain the values of table 2, which are in good agreement with the experimental results.

**Table 2.** Calculated values for the EFG ( $V_{zz}$ ,  $\eta$ ), the electric quadrupole splitting (QS) and the isomer shift with respect to a Pt-metal source (IS) for the  $Au^I$  and  $Au^{III}$  sites in AuSe. Both the values calculated for the atomic positions given in [3] and for optimised positions are listed.

Phase	$V_{zz}^I$ ( $10^{21}/cm^2$ )	$\eta^I$	QS <sup>I</sup> (mm/s)	IS <sup>I</sup> (mm/s)	$V_{zz}^{III}$ ( $10^{21}/cm^2$ )	$\eta^{III}$	QS <sup>III</sup> (mm/s)	IS <sup>III</sup> (mm/s)
$\alpha$ -AuSe	-48.1	0.068	-5.29	1.66	32.1	0.335	3.59	1.85
$\alpha$ -AuSe opt.	-43.3	0.068	-4.77	1.27	30.1	0.316	3.37	1.68
$\beta$ -AuSe	-50.1	0.020	-5.51	1.87	32.4	0.260	3.60	1.91
$\beta$ -AuSe opt.	-47.4	0.025	-5.22	1.67	30.4	0.233	3.37	1.65

## 5. Conclusions

The Mössbauer study confirms that the two gold positions in  $\alpha$ -AuSe and  $\beta$ -AuSe can be attributed to  $Au^I$  and  $Au^{III}$  species. The hyperfine parameters are nearly the same for  $\alpha$ -AuSe and  $\beta$ -AuSe, as can be expected from the similar nearest-neighbour distances [3]. There is good agreement between the experimental results and calculations of the hyperfine parameters by the APO + lo method using the WIEN2k computer code.

## Acknowledgements

Support by the grant IDEI 1382/2008 of the Romanian Ministry of Education and Research is gratefully acknowledged.

## References

- [1] Cranton G E, Heyding, R D, 1968 *Can. J. Chem.* **46** 2637
- [2] Rabenau A, Rau H, Rosenstein G, 1971 *J. Less-Common Metals* **24** 291
- [3] Rabenau A, Schulz H, 1976 *J. Less-Common Metals* **48** 89
- [4] Thomson J O, Obershain F E, Huray P G, Love J C, Burton J, *Phys. Rev B* **11** 1835
- [5] Parish R V, 1985 in: *Mössbauer Spectroscopy in Chemistry* Vol. 1 (ed. G J Long) 577 (Plenum Press New York)
- [6] Prosser H, Wagner F E, Wortmann G, Kalvius G M, Wäppling R, 1975 *Hyperfine Interactions* **1** 25
- [7] Erickson D J, Roberts L D, Burton J W, Thomson J O, 1971 *Phys. Rev. B* **3** 2180
- [8] Schmidbaur H, Hartmann Ch, Wagner F E, 1988 *Hyperfine Interactions* **40** 335
- [9] Palade P, Wagner F E, Filoti G, 2002 *Hyperfine Interactions C* **5** 185
- [10] Blaha P, Schwarz K, Madsen G K H, Kvasnicka D, Luitz J, 2001 *WIEN2k, An Augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties* (Schwarz K, Technische Universität Wien, Austria) ISBN 3-9501031-1-2
- [11] Madsen G K H, Blaha P, Schwarz K, Sjöstedt E, Nordström L, 2001 *Phys. Rev. B* **64** 195134
- [12] Blöchl P E, Jepsen O, Andersen O K, 1994 *Phys. Rev. B* **49** 16223
- [13] Perdew J P, Burke K, Ernzerhof M, 1996 *Phys. Rev. Lett.* **77** 3865
- [14] Palade P, Wagner F E, Filoti, G, 2002 *Hyperfine Interactions C* **5** 185
- [15] Schwerdtfeger P, Bast R, Gerry M C L, Jacob Ch R, Jansen M, Kellö V, Mudring A V, Sadlej A J, Saue T, Söhnle T, Wagner F E, 2005 *J. Chem. Phys.* **122** 124317
- [16] Palade P, Wagner F E, Jianu A D, Filoti G, 2003 *J. Alloys and Compounds* **353** 2