

## MÖSSBAUER SPECTROSCOPY OF THE Ag-Au CHALCOGENIDES PETZITE, FISCHESSERITE AND UYTENBOGAARDTITE

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### ABSTRACT

Mössbauer spectra of the 77.3 keV  $\gamma$  rays of  $^{197}\text{Au}$  were measured at 4.2 K for natural and synthetic  $\text{Ag}_3\text{AuTe}_2$  (petzite), synthetic  $\text{Ag}_3\text{AuSe}_2$  (fischesserite) and synthetic  $\text{Ag}_3\text{AuS}_2$  (uytenbogaardtite). All compounds studied exhibit large gradients in electric field at the gold nuclei, notably the largest so far found in any gold mineral. The isomer shifts and electric quadrupole interactions, and in particular the similarity of these parameters for  $\text{Ag}_3\text{AuS}_2$  with those of  $\text{Au}_2\text{S}$ , suggest that the gold in the  $\text{Ag}_3\text{AuX}_2$  compounds should be considered as monovalent.

**Keywords:** refractory Au minerals, invisible Au, structurally bound Au, Ag-Au chalcogenides, petzite, fischesserite, uytenbogaardtite,  $^{197}\text{Au}$  Mössbauer spectroscopy, isomer shift, electric quadrupole interaction, Hollinger mine, Timmins, Hemlo deposit, Ontario.

### SOMMAIRE

Nous avons étudié les spectres de Mössbauer des rayons  $\gamma$  (77.3 keV) de l'isotope  $^{197}\text{Au}$  générés à 4.2 K et mesurés sur des échantillons naturels et synthétiques de  $\text{Ag}_3\text{AuTe}_2$  (petzite), et des échantillons synthétiques de  $\text{Ag}_3\text{AuSe}_2$  (fischesserite) et  $\text{Ag}_3\text{AuS}_2$  (uytenbogaardtite). Tous ces composés font preuve d'un gradient intense dans le champ électrique autour du nucléus des atomes d'or, et en fait le plus intense qui ait été découvert dans une espèce aurifère. D'après les déplacements isomères et les interactions électriques quadrupolaires, et en particulier la similarité de ces paramètres dans le  $\text{Ag}_3\text{AuS}_2$  avec ceux de  $\text{Au}_2\text{S}$ , l'or dans ces composés  $\text{Ag}_3\text{AuX}_2$  serait monovalent.

(Traduit par la Rédaction)

**Mots-clés:** minéraux réfractaires de l'or, or invisible, or incorporé dans le réseau, chalcogénures de Ag-Au, petzite, fischesserite, uytenbogaardtite, spectroscopie Mössbauer  $^{197}\text{Au}$ , déplacement isomère, interaction électrique quadrupolaire, mine de Hollinger, Timmins, gisement de Hemlo, Ontario.

### INTRODUCTION

Gold occurs in nature as well-defined minerals (native gold, *i.e.*, metallic gold or gold alloys with silver, and compounds, mainly with Te, Bi or Sb), and as a dilute impurity within sulfides (mainly arsenopyrite and pyrite) (Wilson 1982, Harris 1990). Because gold locked up within sulfides

commonly is refractory to conventional techniques of extraction (cyanidization), a better understanding of the mineralogical characteristics of gold and gold-bearing minerals is of great practical significance. Mössbauer spectroscopy can be used to characterize the nature of gold in such materials (Wagner *et al.* 1986, 1988, 1989, Friedl *et al.* 1991). In this context, it is of interest to understand the

Mössbauer spectra of gold in well-defined minerals of gold. As part of a systematic survey of gold minerals by  $^{197}\text{Au}$  Mössbauer spectroscopy, in the present work we report on a study of petzite, fischesserite and uytenbogaardtite. These minerals are silver-gold chalcogenides with the general formula  $\text{Ag}_3\text{AuX}_2$ , where  $X$  stands for Te, Se, and S, respectively (Prince 1988a, b, c).

Petzite ( $\text{Ag}_3\text{AuTe}_2$ ) is the widely occurring natural silver-gold telluride known since 1845. At temperatures below  $320^\circ\text{C}$ , it has a cubic structure (Frueh 1959, Cabri 1965, Chamid *et al.* 1978), comparable with that of garnet. The space group is  $I4_132$ . The rare mineral fischesserite ( $\text{Ag}_3\text{AuSe}_2$ ) was first described in 1971 (Johan *et al.* 1971); below  $270^\circ\text{C}$ , it has a cubic  $I432$  crystal structure, similar to that of petzite. The very rarely occurring mineral uytenbogaardtite ( $\text{Ag}_3\text{AuS}_2$ ) is an analog of petzite and fischesserite. Messien *et al.* (1966) reported the low-temperature form of  $\text{Ag}_3\text{AuS}_2$  (stable below  $185^\circ\text{C}$ ) to be cubic, but Graf (1968), Smit *et al.* (1970) and Barton *et al.* (1978) later demonstrated that the symmetry of the room-temperature modification is actually tetragonal,  $P4_122$  or  $P4_1$ . The observed reflections show that the space group is primitive and that the only possible elements of non-unit translational symmetry are a  $4_1$  or a  $4_2$  axis. Despite these differences, the crystal structures of the three minerals are closely related. The packing of anions is approximately body-centered: gold is coordinated by two, silver by four chalcogen atoms distributed in a tetrahedron. Gold atoms are located on the  $1/8$ ,  $1/8$ ,  $1/8$ , *etc.*, positions in the cubic (or almost cubic) unit-cell, which contains eight gold atoms. Each gold atom has two close Te, Se or S neighbors ("dumbbell") located along the body diagonal, and six Ag atoms as next-nearest neighbors. Because of this linear two-fold coordination, the environment of gold in these minerals is very different from that, for instance, of the gold-silver ditellurides, in which there is a six-fold coordination of Te atoms to the gold. Also, the distance between Au and its nearest neighbors,  $2.61 \text{ \AA}$  in petzite (Chamid *et al.* 1978), is markedly shorter than any bond length in the gold ditellurides (Tunell & Pauling 1952, Pertlik 1984a, b, c).

The information about the chemical state of gold obtained by Mössbauer spectroscopy stems mainly from the electric quadrupole interaction and from the isomer shift of the Mössbauer pattern. The former splits the Mössbauer line of  $^{197}\text{Au}$  into a doublet whose separation, the quadrupole splitting (QS), depends on both the symmetry and the degree of covalency of the bonds between the gold atoms and their ligands. The isomer shift (IS) is a measure of the electron density at the gold nuclei. Both the electron density at the gold nuclei and the isomer

shift increase with the valence state of gold and with the covalency of the bonds between the gold and its ligands. For the linear, two-fold-coordinated  $\text{Au}^+$  compounds as well as for the planar four-fold-coordinated  $\text{Au}^{3+}$  compounds, distinctive approximately linear correlations between the electric quadrupole splitting and the isomer shift have been found (Bartunik *et al.* 1970, Faltens & Shirley 1970). Using these correlations, one can determine the valence state of gold in such compounds from the observed values of the isomer shift and the quadrupole splitting. For bonding situations that deviate from the two-fold linear or four-fold planar coordination, however, a distinction between  $\text{Au}^+$  and  $\text{Au}^{3+}$  on the basis of Mössbauer spectroscopy may be difficult, the more so since one normally cannot determine the sign of the electric quadrupole interaction, which is expected to be negative for linear  $\text{Au}^+$  and positive for planar  $\text{Au}^{3+}$  compounds (Parish 1982, 1984).

#### EXPERIMENTAL

Mössbauer spectra of petzite have been measured for two natural and three synthetic specimens. One of the natural specimens is a 5-mm-thick slab of rock from the Golden Spectre property, Hemlo, Ontario. The specimen contains small inclusions of petzite, intergrown with hessite ( $\text{Ag}_2\text{Te}$ ) and chalcopyrite ( $\text{CuFeS}_2$ ), highly disseminated in quartz and K-feldspar. It also contains a large amount of native gold. The second natural specimen consists of single-crystal pieces with a total volume of about  $10 \text{ mm}^3$ , which were extracted from ore of the Hollinger mine, Timmins, Ontario. This specimen was obtained from the Royal Ontario Museum, where it is registered as M13740. It contains a very small amount of visible native gold. Unfortunately, we could not obtain natural specimens containing fischesserite and uytenbogaardtite in quantities measurable by Mössbauer spectroscopy.

A synthetic specimen of petzite was obtained from the Royal Ontario Museum, where it is registered as R395. The specimens produced in the course of this work were made by fusing the elements in the required stoichiometric amounts in evacuated and sealed quartz tubes. In the case of  $\text{Ag}_3\text{AuTe}_2$  and  $\text{Ag}_3\text{AuSe}_2$ , the charges were melted at  $1000^\circ\text{C}$  for 12 hours. After grinding and sealing again, the specimens were annealed at  $900^\circ\text{C}$  for 24 hours and then cooled from  $900^\circ\text{C}$  to  $700^\circ\text{C}$  for 6 days. Two specimens of  $\text{Ag}_3\text{AuS}_2$  were prepared by heating to  $1200^\circ\text{C}$  for 12 hours. The first of them was prepared with the exact stoichiometric proportions of the elements, whereas in the preparation of the second one, excess sulfur was included. The temperature of the synthesis seems

TABLE 1. UNIT-CELL DATA OBTAINED FOR THE  $Ag_3AuS_2$  (X=Te, Se, S) COMPOUNDS STUDIED IN THE PRESENT WORK\*

COMPOUND	SPACE GROUP	a (Å)	c (Å)	V (Å <sup>3</sup> )	REFERENCE
$Ag_3AuTe_2$	$I4_132$	10.3850(4)	-	1120	Chamidi <i>et al.</i> (1978)
	cubic	10.338(4)	-	1105	this work, R395
$Ag_3AuSe_2$	$I432$	9.967(3)	-	990	Johan <i>et al.</i> (1971)
	cubic	9.974(1)	-	992	this work, synth. 1000°C
$Ag_3AuS_2$	$P4_122$ or $P4_1$	9.68	9.81	919	Barton <i>et al.</i> (1978)*
	tetragonal	9.71(1)	9.80(4)	925	this work, synth. 500°C

\*The references refer to the recent crystallographic work on the respective minerals.  
 \*The cell edges of one of two specimens (Tembang Sawah) are quoted; experimental errors were not given in the reference.

to have been too high, as in both cases a significant amount of sulfur did not react. Thus, the third specimen of  $Ag_3AuS_2$  was prepared at 500°C for 100 hours and then cooled to room temperature during 20 hours. This procedure also was used to prepare a sample of petzite. The chemical composition of the specimens was determined by electron-microprobe analysis, which showed significant fractions of native gold in petzite and in the uyttenbogaardtite synthesized at high temperatures. The indexing of the X-ray powder-diffraction photographs yielded good agreement of the unit-cell parameters with the published structural data (Table 1). The results of electron-microprobe analysis of the native gold inclusions present in the specimens are in fair agreement with the calculated

compositions of the gold-silver alloys derived from the Mössbauer spectra.

The 18-h-half-life  $^{197}Pt$  sources for the  $^{197}Au$  Mössbauer measurements were prepared by irradiation of about 200 mg of enriched  $^{196}Pt$  metal in a neutron flux of  $2 \times 10^{13}$  n/s-cm<sup>2</sup> for one day. The Mössbauer  $\gamma$ -rays were detected with a planar intrinsic Ge detector, which yielded count rates of up to  $2 \times 10^5$ /s in the window of the single-channel analyzer set on the 77.3 keV line. The absorbers of synthetic specimens were fine powders distributed uniformly over an area of 2 cm<sup>2</sup>. The absorber thickness was between about 60 and 200 mg/cm<sup>2</sup>. The gold content of the petzite-bearing slab of rock was not determined, but was sufficient for measurement of a Mössbauer spectrum. All measurements were performed with both the source and the absorber cooled to 4.2 K in a liquid He bath cryostat. The spectra were least-squares-fitted with superpositions of Lorentzian lines. All line positions and isomer shifts are given with respect to the source, *i.e.*, to  $^{197}Au$  in Pt metal. In order to convert them to shifts relative to metallic gold, 1.23 mm/s must be added to the given values.

RESULTS

The  $^{197}Au$  Mössbauer spectra of some of the specimens are shown in Figure 1, and the relevant Mössbauer parameters are compiled in Table 2.

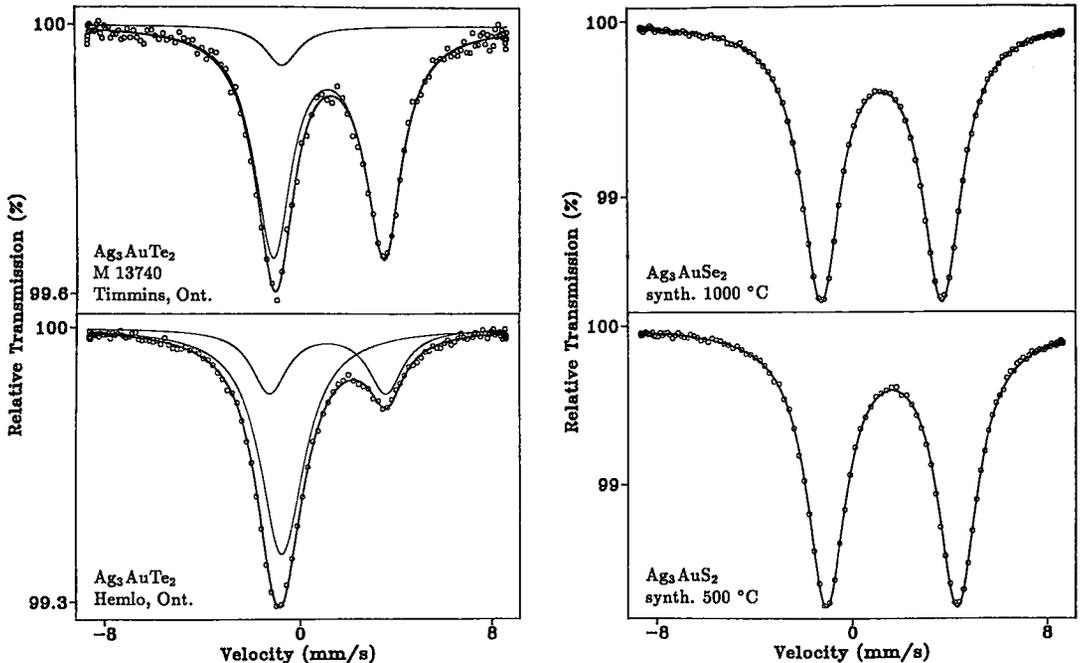


FIG. 1.  $^{197}Au$  Mössbauer spectra of petzite ( $Ag_3AuTe_2$ ), fischerite ( $Ag_3AuSe_2$ ) and uyttenbogaardtite ( $Ag_3AuS_2$ ).

TABLE 2. MÖSSBAUER RESULTS FOR THE INVESTIGATED GROUP OF MINERALS\*

ABSORBER	IS (mm/s)	QS (mm/s)	W (mm/s)	RI(%)	REMARKS
Peztite $Ag_3AuTe_2$					
Timmins, Ont. (M13740)	+1.19(2) -0.68(16)	4.56(5) -	1.85(4) 1.88(40)	92(2) 8(2)	Au* Au <sub>76</sub> Ag <sub>24</sub>
Hemlo, Ont.	+1.14(4) -0.74(2)	4.80(7) -	1.78(8) 2.20(5)	31(1) 69(1)	Au* Au <sub>78</sub> Ag <sub>22</sub>
Synthetic (R395)	+1.18(4) -0.75(9)	4.58(7) -	1.90(5) 2.01(20)	75(2) 25(2)	Au* Au <sub>79</sub> Ag <sub>21</sub>
Synthetic (1000°C/12 h)	+1.12(1) -0.59(1)	4.80(4) -	1.68(3) 2.30(2)	20(1) 80(1)	Au* Au <sub>72</sub> Ag <sub>28</sub>
Synthetic (500°C/100 h)	+1.12(3) -0.81(4)	4.52(6) -	2.14(4) 2.33(8)	56(1) 44(1)	Au* Au <sub>80</sub> Ag <sub>20</sub>
Fischesserite $Ag_3AuSe_2$					
Synthetic (1000°C/12 h)	+1.20(1)	4.96(3)	1.84(2)	100	Au*
Uytenbogaardite $Ag_3AuS_2$					
Synthetic (1200°C/12 h)	+1.57(2) -0.63(8)	5.38(4) -	1.94(4) 2.05(17)	79(1) 21(1)	Au* Au <sub>74</sub> Ag <sub>26</sub>
Synthetic (1200°C/12 h)	+1.60(2) -0.54(3)	5.42(5) -	1.96(9) 2.58(8)	64(1) 36(1)	Au* Au <sub>70</sub> Ag <sub>30</sub>
Synthetic (500°C/100 h)	+1.59(1)	5.36(3)	1.96(2)	100	Au*

\*IS is the isomer shift relative to the source of Au in Pt metal, QS is the electric quadrupole splitting, W the FWHM line width, and RI the relative intensity of the respective components. Figures in brackets indicate uncertainty in last digit(s) reported.

### Peztite

The spectra of the five different specimens of peztite exhibit two well-separated absorption lines. The different intensities of the two resonant lines can be attributed to the presence of different amounts of native gold (electrum) in the different specimens. The right-hand peak is always at virtually the same position, + 3.48 ± 0.03 mm/s, and has nearly the natural linewidth. The left-hand peak is always more intense and slightly broadened, which indicates that it is composed of the left peak of a quadrupole doublet attributable to peztite and a peak due to impurities of a gold-silver alloy. The left-hand peak of peztite should be at the same place in all cases, whereas the position of the alloy peak may vary with the Au/Ag ratio, since Au-Ag alloys have a more positive isomer shift (Huray *et al.* 1976) than pure gold with its resonance line at -1.23 mm/s. These considerations leave only the disposition of lines as shown in Figure 1 for the consistent fitting of all of the peztite spectra. The Timmins specimen (M13740) yielded the spectrum with the weakest line for the gold-silver alloy. We therefore consider the Mössbauer parameters of peztite obtained for this sample (IS = +1.19 mm/s, QS = 4.56 mm/s) as the most reliable that can presently be given.

The relative intensities (RI) of the peztite and

gold-silver alloy components given in Table 2 refer to the areas of the respective components in the Mössbauer spectra. The relative amounts of peztite and gold-silver alloy may be different from these values because the Lamb-Mössbauer f-factors of the two components may differ somewhat. In the course of this work, no efforts were made to measure the ratio of these f-factors.

The composition of the gold-silver alloys observed in the spectra can be estimated using an empirical linear relationship between the content of silver, x, in  $Au_{100-x}Ag_x$  alloys and the isomer shift IS of the Mössbauer line (Huray *et al.* 1976), which can be written as

$$x[\text{at.}\%] = 44 \cdot (\text{IS}[\text{mm/s}] + 1.23).$$

The compositions given in Table 2 have been derived from this relation and the observed isomer shifts. Note that the composition of the metallic phase in both the peztite and the uytenbogaardite samples is always much richer in gold than the nominal Au/Ag ratio in these specimens ( $AuAg_3$ ). This seems to be a systematic deviation, the alloy phase being always about  $Au_3Ag$  whatever the total amount of gold present in the metallic form. The excess silver is presumably bound in a silver telluride such as hessite ( $Ag_2Te$ ), which is invisible to Mössbauer spectroscopy.

### Fischesserite

The  $^{197}\text{Au}$  spectrum of synthetic  $Ag_3AuSe_2$  exhibits a symmetrical quadrupole doublet and shows no trace of a gold-silver alloy. The Mössbauer parameters of this doublet are very close to those of peztite (Table 2).

### Uytenbogaardite

The Mössbauer spectrum of the synthetic  $Ag_3AuS_2$  sample prepared at 500°C is symmetrical and shows no traces of impurities, whereas the specimens prepared at 1200°C contain some gold-silver alloy. Fits in analogy to those for the peztite spectra yield the results given in Table 2.

## DISCUSSION

The common feature of the Mössbauer spectra of the three compounds investigated is a rather large quadrupole splitting (QS ≈ 4.5–5.4 mm/s). Large magnitudes of the quadrupole splitting, which is a measure of the gradient in the electric field at the Au nuclei, are in accordance with the linear two-fold coordination of the gold atoms expected from the similarity of the cell edges in all three compounds, although a determination of the atomic position so far has been made only for peztite. The similarity of the Mössbauer parameters

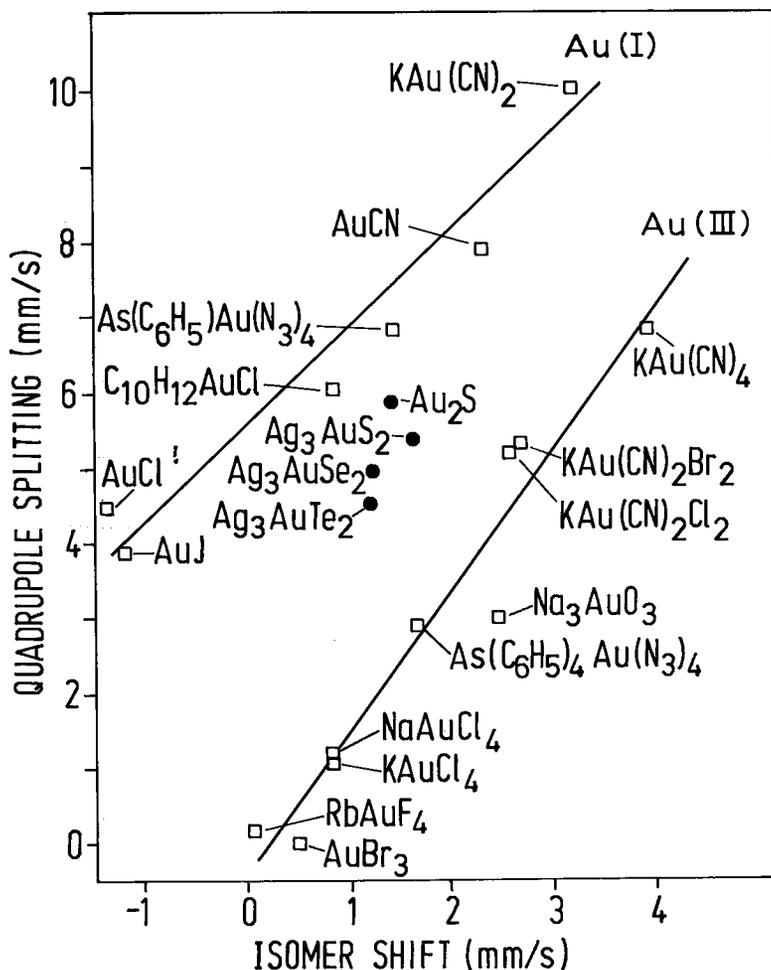


FIG. 2. Plot of the magnitude of the electric quadrupole splitting versus the isomer shift (relative to gold in a platinum matrix) for  $\text{Au}^+$  and  $\text{Au}^{3+}$  compounds, as well as the gold minerals studied in the present work.

of all three compounds in the  $\text{Ag}_3\text{AuX}_2$  series confirms that the coordination of gold is very similar in all three cases. On the basis of the known, approximately linear relation between IS and QS in covalent auric and aurous compounds (Bartunik *et al.* 1970, Parish 1982, 1984), of which a part is shown in Figure 2, one finds the investigated compounds to be between the  $\text{Au}^+$  and the  $\text{Au}^{3+}$  regions. In both valence states, the IS and QS increase as the gold-ligand bonds become more covalent, and greater electron density is placed on the gold atom. An unambiguous distinction between  $\text{Au}^+$  and  $\text{Au}^{3+}$  could be made if the sign of the gradient in the electric field could be determined, since the gradients are expected to be negative in the  $\text{Au}^+$  and positive in the  $\text{Au}^{3+}$

compounds (Parish 1984). In the present case, however, only the magnitudes of the quadrupole interaction can be determined from the Mössbauer spectra of powder absorbers. Even oriented single-crystal specimens, which normally allow the sign of the quadrupole interaction to be determined (Prosser *et al.* 1975), would not be helpful in the present case, where the cubic ( $\text{Ag}_3\text{AuTe}_2$  and  $\text{Ag}_3\text{AuSe}_2$ ), or at least nearly cubic ( $\text{Ag}_3\text{AuS}_2$ ) symmetry would preclude a net alignment of the tensors of the gradient in the electric field in the absorber, and hence the determination of the sign of the electric quadrupole interaction. However, the linear coordination of the gold between its two nearest tellurium neighbors in  $\text{Ag}_3\text{AuTe}_2$  (Frueh 1959), together with its position in the plot of the

quadrupole splittings *versus* the isomer shifts (Fig. 2), strongly support the notion that gold in petzite is monovalent. From the similarity of the Mössbauer parameters of petzite, fischesserite and uytenbogaardtite, one then concludes that the same is true for the oxidation state of the gold in the latter two minerals. This view is supported by the similarity of Mössbauer parameters of  $\text{Ag}_3\text{AuS}_2$  with those of the  $\text{Au}^+$  compound  $\text{Au}_2\text{S}$  (Faltens & Shirley 1970), which has the  $\text{Cu}_2\text{O}$  type structure ( $\text{O}_h4$ ,  $\text{Pn}3m$ ) (Hirsch *et al.* 1966), in which the gold is linearly coordinated to two neighboring sulfur atoms at a distance of 2.17 Å. Figure 2 shows that  $\text{Au}_2\text{S}$  also falls between the  $\text{Au}^+$  and  $\text{Au}^{3+}$  regions on the QS *versus* IS plot and is remarkably close to  $\text{Ag}_3\text{AuS}_2$ , which indicates very similar bonding situations and gold-sulfur distances.

The Au-Te distances are 2.61 Å in petzite (Chamid *et al.* 1978). Because of the smaller size of the unit cell, the distances between Au and Se in fischesserite are expected to be smaller than the Au-Te distances in petzite. This may be the reason for the larger quadrupole splitting. The quadrupole splitting along the series  $\text{Ag}_3\text{AuTe}_2 - \text{Ag}_3\text{AuSe}_2 - \text{Ag}_3\text{AuS}_2$  increases with decreasing unit-cell volume, and hence with decreasing gold-chalcogen distance. It is tempting to attribute this to increasing covalency, with the Au-S bond being the most covalent. It is, however, difficult to decide to what extent the increasing covalency is attributable to the nature of the ligands and to what extent it is attributable to the decreasing bond-length of the gold-ligand bond.

The difference in isomer shifts between pure Au metal (IS = -1.23 mm/s) and the  $\text{Ag}_3\text{AuX}_2$  (IS ≈ +1.2-1.6 mm/s) shows that the density of electrons at the Au nucleus in the  $\text{Ag}_3\text{AuX}_2$  compounds is larger than that of Au metal. The observed magnitude of the isomer shift in petzite (IS = +1.2 mm/s) is only slightly smaller than in gold-silver ditellurides (IS ≈ +1.4-1.7 mm/s) (Wagner *et al.* 1986, 1988). The explanation of the smaller values of the isomer shift, and thus smaller charge-transfer from tellurium to gold atoms, may rest in the fact that in the ditellurides, the gold atoms are bonded to six fairly close tellurium atoms, whereas in petzite the gold has only two close neighbors. In addition, whereas most of the other phases in the system Ag-Au-Te have metallic bonding, conductivity data suggest that covalent bonding is of considerable significance in petzite (Rucklidge & Stumpfl 1968).

#### CONCLUSIONS

The electric quadrupole interactions observed in  $\text{Ag}_3\text{AuX}_2$  compounds are the largest so far found in any gold mineral. In particular, its large

quadrupole splitting allows petzite to be easily distinguished from the ditelluride minerals calaverite, sylvanite and krennerite. Notably, the Mössbauer analyses can be made on rather large pieces of rock without separation of the gold mineral, as long as the overall content of gold in the sample exceeds about 100 ppm.

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