^{197}AU, ^{57}Fe AND ^{121}Sb MÖSSBAUER STUDY OF GOLD MINERALS AND ORES

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A survey of the ^{197}Au Mössbauer spectra of naturally occurring gold species is given. Gold minerals have been studied as natural specimens or as synthetic analogues. Gold impurities have been identified in pyrites and arsenopyrites. An example of the use of ^{121}Sb and ^{57}Fe Mössbauer spectroscopy in characterizing gold-bearing ore minerals is given.

1. Introduction

The use of complex sulfidic ores for commercial gold production has increased considerably in recent years. A knowledge of the state of gold in such materials is important for designing improved methods of gold recovery, but both optical and electron microscopy often fail to yield the required information because the gold is either too finely distributed to be visible or chemically bound as an impurity in various host minerals [1,2]. Such gold often cannot be extracted by cyanidation without previous steps of beneficiation, such as roasting or bacterial oxidation. During recent years, Mössbauer spectroscopy with the 77 keV resonance in ^{197}Au has emerged as a useful method for studying the chemical state of gold in such ores [3–7]. Mössbauer spectra of sulfidic ores can presently be measured with good statistical accuracy down to gold concentrations of about 50 ppm. However, the analytical power of Mössbauer spectroscopy largely depends on reference data for well-characterized materials. For quantitative analyses, the Lamb-Mössbauer f-factors of gold in different bonding states are also needed. In the following, we will present such data as well as an example of the use of ^{121}Sb and ^{57}Fe Mössbauer spectroscopy in the characterization of natural, gold-bearing ore minerals.

2. ^{197}Au Mössbauer data for gold minerals and ores

Data for gold minerals and a selection of results for gold ores and alloys are compiled in Table 1. Natural mineral specimens were studied whenever available; otherwise synthetic

Table 1

^{197}Au Mössbauer parameters of some gold alloys, of gold minerals, and of the combined gold observed in pyritic and arsenopyritic gold ores. *IS* is the isomer shift with respect to a source of metallic platinum, *QS* the electric quadrupole splitting, f/f_{Au} the Lamb-Mössbauer factor relative to that of metallic gold, and *RI* the relative intensity (area) of a component in the spectrum.

Material	*IS* (mm/s)	*QS* (mm/s)	f/f_{Au}	*RI* (%)
Metallic gold and gold alloys				
Au	−1.22 (1)	—	1.0	100
$Au_{0.01}Ag_{0.99}$	+0.68 (1)	—	0.95 (2)	100
$Au_{0.01}Cu_{0.99}$	+2.76 (2)	—	1.33 (2)	100
Gold minerals (synthetic specimens are denoted by an asterisk)				
$AuTe_2$ (calaverite)	+1.97 (3)	2.43 (3)		63 (2)
	+0.42 (4)	1.77 (5)		27 (2)
$Au_{0.2}Ag_{0.8}Te_2$ (krennerite)	+1.54 (2)	2.75 (2)		63 (2)
	+0.14 (4)	2.08 (6)		27 (2)
$AuAgTe_4$ (sylvanite)	+1.71 (1)	2.64 (2)		91 (1)
	−0.78 (7)	1.01 (14)		09 (1)
$AuCuTe_4$ (kostovite)*	+1.61 (1)	2.56 (2)		85 (1)
	+0.15 (2)	2.01 (3)		15 (1)
$(Au,Sb)_2Te_3$ (montbrayite)	+1.48 (1)	2.31 (2)		58 (1)
	+0.57 (2)	1.90 (2)		42 (1)
Ag_3AuTe_2 (petzite)	+1.19 (2)	4.56 (4)		100
Ag_3AuSe_2 (fischesserite)*	+1.20 (1)	4.96 (1)		100
Ag_3AuS_2 (uytenbogaardtite)*	+1.60 (1)	5.42 (1)		100
$Pb_5Au(Te,Sb)_4S_{5-8}$ (nagyagite)	+1.67 (1)	3.56 (1)		100
$AuSb_2$ (aurostibite)	+2.33 (2)	—		100
$TlAg_2Au_3Sb_{10}S_{10}$ (criddleite)*	+2.36 (1)	—		100
Au_2Bi (maldonite)*	+0.07 (1)	3.31 (2)		100
Gold in ore concentrates (nonmetallic components only)				
Au:FeS_2 (≈90 ppm)[1]	+2.49 (5)	—	1.85 (35)	91 (2)
Au:FeS_2 (≈50 ppm)[2]	+3.13 (9)	—		100
Au:FeS_2 (≈100 ppm)[3]	+3.49 (7)	—	1.64 (30)	100
Au:FeS_2 (≈400 ppm)[4]	+4.01 (6)	—		34 (2)
Au:FeAsS (≈160 ppm)[5]	+3.28 (5)	—		100
Au:FeAsS (1800 ppm)[6]	+3.53 (1)	—	1.45 (4)	100
Au:FeAsS (≈150 ppm)[7]	+3.62 (3)	—	1.46 (6)	100
Au:FeAsS (6400 ppm)[8]	+3.62 (2)	—		77 (1)

Origin: [1] Columbia; [2] Golden Bear Deposit, Northwestern British Columbia, Canada; [3] Villeranges, France; [4] Newhawk Gold Mines, Northern British Columbia, Canada; [5] Barbrook Mine, Eastern Transvaal, South Africa; [6] Le Châtelet, Creuse, France; [7] New South Wales, Australia (cf. ref. [6]); [8] Synthetic, prepared as described in refs. [16,17]).

analogues were prepared. The ore concentrates containing chemically bound gold listed in Table 1 are pyrites, arsenopyrites, or mixtures thereof in which the gold is mainly contained in the arsenopyrite. Data for a synthetic gold-bearing arsenopyrite are also included.

The Mössbauer spectra of most gold minerals are electric quadrupole doublets or single lines. Two doublets are required to fit the spectra of the ditellurides. In $AuTe_2$ and

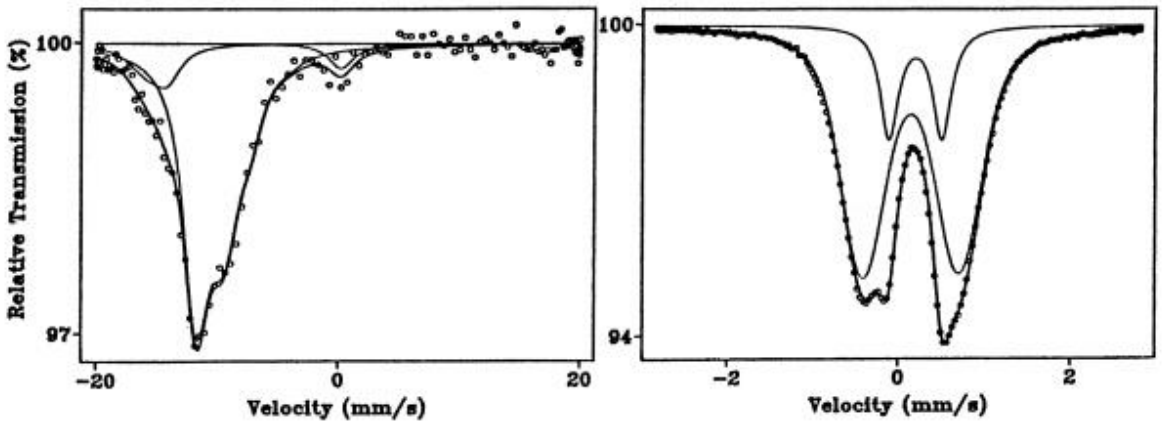

Fig. 1: ^{121}Sb (left) and ^{57}Fe (right) Mössbauer spectra of a gold ore concentrate consisting of a mixture of arsenopyrite and pyrite. The ^{121}Sb spectrum was taken at 4.2 K with a source of $Ba^{121}SnO_3$, the ^{57}Fe spectrum at 300 K with a source of ^{57}Co in Rh.

$Au_{0.2}Ag_{0.8}Te_2$ this is justified by the presence of two crystallographically different gold sites [8]. In $AuAgTe_4$ and $AuCuTe_4$, the weak second doublet must be attributed to deviations from stoichiometry or to disorder between the Au and Ag (or Au and Cu) sublattices. The spectrum of montbrayite ($(Au,Sb)_2Te_3$, [9]) is similar to that of calaverite. The studied criddleite was the synthetic material that had also been used in the characterization of this mineral [10]. The f factors given in Table 1 were determined relative to that of metallic gold (f = 0.188(1) [11]) from simultaneous measurements with a reference absorber. Since the gold content of ore concentrates is usually not known very accurately, the f factors of these materials were determined by a method that does not rely on an independent determination of the gold content [6]. The ^{197}Au Mössbauer spectra of gold in pyrites and arsenopyrites often consist of a metallic component and of a pattern arising from chemically bound gold. The latter gives rise to somewhat broadened, sometimes slightly asymmetric lines with no clear quadrupole splitting. For pyrite, the centre shifts cover a rather wide range of values between about +2.5 and +4.0 mm/s; the shifts for arsenopyrites fall into a narrower range between about +3.2 and to +3.7 mm/s. In the pyrites listed in Table 1 no FeAsS could be detected by ^{57}Fe Mössbauer spectroscopy, which sets an upper limit of about 0.5% for the FeAsS content, but elementary analyses [12–13] usually reveal the presence of several thousand ppm of As in the pyrite lattice. Unless the gold in FeS_2 is contained in rare but very gold-rich micro-inclusions of FeAsS, it presumably replaces Fe in the FeS_2 lattice. The range of isomer shifts for Au in pyrite could then arise from As impurities clustering near the Au solutes. In arsenopyrite, the environment of the gold substituting for iron would be subject to smaller variations arising from non-stoichiometry and disorder.

3. ^{121}Sb and ^{57}Fe Mössbauer spectroscopy

Gold-bearing arsenopyrite often contains percent amounts of antimony [12–14]. Johan et al. [14] suggested that antimony occupies iron sites in FeAsS, but a replacement of arsenic or sulfur by Sb cannot be ruled out. ^{121}Sb Mössbauer spectroscopy can help to answer such questions. Fig. 1 shows the ^{121}Sb and ^{57}Fe spectra of a concentrate from Le Châtelet, France (cf. Table 1), which contains about 1 wt.% Sb, and in which, according to the iron Mössbauer spectrum, 32% of the iron is bound in FeS_2 and 68% in FeAsS. The ^{121}Sb spectrum contains a weak contribution of stibnite (Sb_2S_3) and a very weak Sb(V) component, but the majority of

the antimony yields a narrow quadrupole pattern with Mössbauer parameters ($IS = -10.2(1)$ mm/s with respect to the $BaSnO_3$ source, $eQV_{zz} = -15.4(4)$ mm/s, $\eta = 0$) that are very close to those found for ^{121}Sb in FeSbS, the mineral gudmundite ($IS = -10.0(1)$ mm/s, $eQV_{zz} = -15.6(2)$ mm/s, $\eta = 0$), which has an arsenopyrite-type structure [15] in which the antimony is tetrahedrally coordinated to one sulfur and three iron neighbours, as is arsenic in FeAsS. This strongly suggests that Sb in arsenopyrite replaces arsenic.

Conclusions

We have presented Mössbauer data for gold minerals, which will be useful in the interpretation of the spectra of natural gold-bearing materials. We have also shown that ^{121}Sb Mössbauer spectroscopy can be used to study the chemical state of trace amounts of antimony in such materials, while ^{57}Fe Mössbauer spectroscopy may be considered a standard method for characterizing the state of the iron that is usually a major constituent of gold ores.

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