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^{197}Au Mössbauer Spectroscopic Study of the Ternary Systems $(Ag,Au)_2X$ (X=S and Se)

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^{197}Au Mössbauer spectroscopy has been applied for the low-temperature β-phases of ternary systems, $Ag_{2-x}Au_xX$ (X=S, and Se; x=0.2 and 0.5). The nature of linear X-Au-X bonds present in these systems is discussed on the basis of the Mössbauer data and the bond distances.

The silver chalcogenides, Ag_2X (X=S, Se, and Te), have been extensively studied because of their interesting phase-transition phenomena and electrical properties. The Ag^+ ions are statistically distributed over the cation sites in the three-dimensional frameworks of X^{2-} ions in the high-temperature α-phases of these compounds. In the silver-gold-chalcogen ternary systems, $(Ag,Au)_2X$ (X=S, Se, and Te), stoichiometric compounds, Ag_3AuS_2, AgAuS, Ag_3AuSe_2, and Ag_3AuTe_2, are known to exist as the stable compounds at room temperature.$^{1)}$ These compounds transform to the high-temperature α-phase of the cubic structure, similar to the binary systems Ag_2X. In order to elucidate the charge density and the bond nature of the cation, the ^{197}Au Mössbauer spectroscopy has been first applied for the ternary systems $(Ag,Au)_2X$ (X=S and Se).

Powder samples of $Ag_{2-x}Au_xX$ (X=S and Se; x=0.2 and 0.5) were prepared by heating the appropriate stoichiometric quantities of the elements in an evacuated quartz tube at 700 °C for 24 h. All products were identified by X-ray powder diffraction (XRD) using graphite monochromated Cu-Kα radiation, and characterized by differential thermal analysis (DTA) and differential scanning calorimetry (DSC). ^{197}Au Mössbauer spectra were measured by cooling a ^{197}Pt source and an absorber at 16 K. The ^{197}Pt source was prepared by neutron-irradiation of a 140 mg ^{196}Pt metal (98% enriched) at a fluence rate of $2 \times 10^{13}\ cm^{-2}s^{-1}$ for 1 h in Kyoto University Reactor (KUR). The 77.3 keV Mössbauer γ-ray was detected with a 5 mm-thick

NaI(Tl) scintillation counter. The velocity calibration was performed with an α-Fe spectrum.

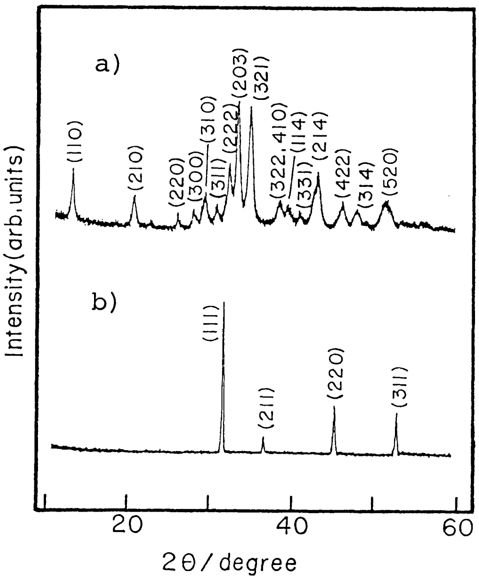

Fig. 1. XRD patterns of Ag_3AuS_2; a) β-phase and b) α-phase.

Figure 1(a) and (b) shows typical XRD patterns for the low-temperature β-phase (measured at room temperature) and the high-temperature α-phase (at 210 °C) of Ag_3AuS_2. The pattern of the β-phase is well assigned to a tetragonal unit cell with a lattice parameter a=9.75 Å, c=9.85 Å, while that of the α-phase is indexed in a simple cubic a=4.93 Å. The results well agree with those reported by Graf$^{2)}$ and Folmer et al.$^{3)}$ The XRD pattern at room temperature of $Ag_{1.8}Au_{0.2}S$ suggests that the β-phase consists of a mixture of Ag_3AuS_2 and Ag_2S. In the α-phase measured at 130 °C, however, the pattern is assigned to a single phase of a body-centered cubic a=4.89 Å. The phase-transition phenomena of selenides, Ag_3AuSe_2 and $Ag_{1.8}Au_{0.2}Se$, are quite similar to those of the sulfides, in good agreement with the results reported by Messien and Baiwir$^{4)}$ and Wiegers.$^{5)}$

^{197}Au Mössbauer spectra at 16 K for the β-phases of $Ag_{2-x}Au_xS$ (x=0.2 and 0.5) are shown in Fig. 2. The spectra were analyzed with a quadrupole doublet by the least-squares method. The values of the isomer shift (I.S.) relative to the Pt source, the quadrupole splitting (Q.S.), and the line width (Γ) obtained by the best-fitting are given in Table 1. The I.S. and Q.S. values of $Ag_{1.8}Au_{0.2}S$ are close to those of Ag_3AuS_2, suggesting that the charge state and the coordination of the Au atoms in $Ag_{1.8}Au_{0.2}S$ are similar to those in Ag_3AuS_2. This is consistent with the results of the XRD patterns; $Ag_{1.8}Au_{0.2}S$ is a mixture of Ag_3AuS_2 and Ag_2S. In Fig. 3 and Table 1, Mössbauer spectra at 16 K and Mössbauer parameters for the β-phases of $Ag_{2-x}Au_xSe$ (x=0.2 and 0.5) are given. The similar I.S. and Q.S. values between $Ag_{1.8}Au_{0.2}Se$ and Ag_3AuSe_2 suggest that $Ag_{1.8}Au_{0.2}Se$ is a mixture of Ag_3AuSe_2 and Ag_2Se. It is apparent from the values of I.S. and Q.S. that the gold atoms exist as monovalent cations in the sulfides and the selenides.

The crystal structures of the β-phases of Ag_3AuS_2 and Ag_3AuSe_2 have

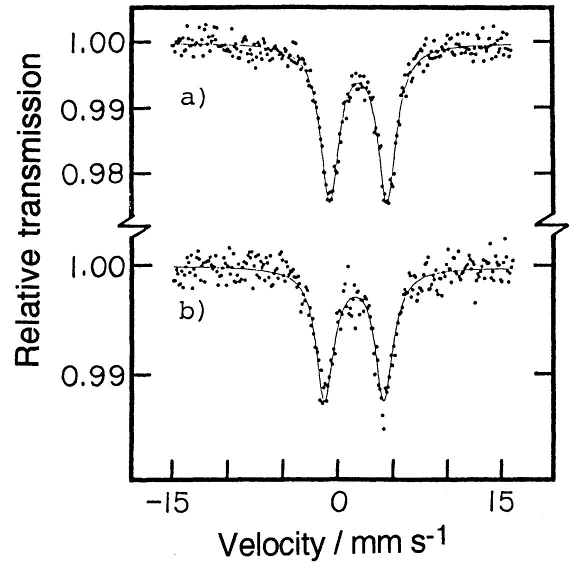

Fig. 2. ^{197}Au Mössbauer spectra at 16 K of a) $Ag_{1.8}Au_{0.2}S$ and b) Ag_3AuS_2.

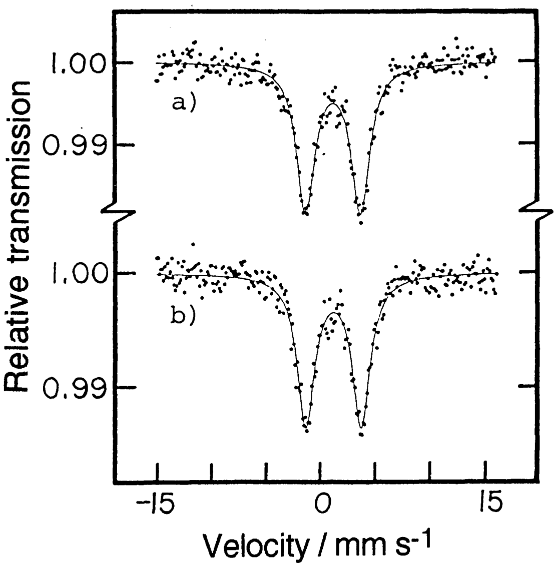

Fig. 3. ^{197}Au Mössbauer spectra at 16 K of a) $Ag_{1.8}Au_{0.2}Se$ and b) Ag_3AuSe_2.

Table.1 Mössbauer data at 16 K of sulfides and selenides

Samples	I.S.[a] / mm s^{-1}	Q.S. / mm s^{-1}	Γ / mm s^{-1}
$Ag_{1.8}Au_{0.2}S$	1.65 ± 0.05	5.43 ± 0.05	2.12 ± 0.08
Ag_3AuS_2	1.56 ± 0.05	5.38 ± 0.05	1.95 ± 0.08
$Ag_{1.8}Au_{0.2}Se$	1.28 ± 0.05	4.99 ± 0.05	2.06 ± 0.08
Ag_3AuSe_2	1.25 ± 0.05	5.00 ± 0.05	1.94 ± 0.08

a) The I.S. values are relative to the Pt source.

determined by Messien et al.6) and Messien and Baiwir.4) The crystallographic data suggest that the anion packings are approximately body-centered, the silver atoms are coordinated by four chalcogen atoms, and the gold atoms are linearly coordinated by two chalcogen atoms. The linear coordination is observed for a large number of Au(I) compounds. The linear S-Au-S bond in β-Ag_3AuS_2 is unsymmetric, involving two Au-S bond distances of 2.76 Å and 2.94 Å. On the other hand, in β-Ag_3AuSe_2 two Au-Se bonds are of equal distance of 2.56 Å. The distance is much less than the sum of respective ionic radii (3.35 Å for Pauling's scale), which predicts substantial covalent character for the Au-Se bond.

As seen in Table 1, the values of I.S. and Q.S. for β-Ag_3AuSe_2 are smaller than those for β-Ag_3AuS_2. This result suggests in general that the covalent character of the Au-Se bond is smaller than that of the Au-S bond,7) contrary to the expectation based on the bond distance. The conflict may be resolved by considering the differences in the bond nature between Se-Au-Se and S-Au-S. In the case of Au(I), the $5d_{z^2}$, 6s, and $6p_z$ atomic orbitals of gold are suitable for σ-bonding.8) It is likely from the abnormally short distance of the Au-Se bonds that two 6s6p hybrid orbitals mixed with substantial $5d_{z^2}$ character are used for the bond formation. The participation of the $5d_{z^2}$ orbital of gold to the σ-bonding leads to a decrease in the quadrupole splitting mainly attributable to $6p_z$ populations, because of opposite contribution to the electric field gradient. On the other hand, the large I.S. value for β-Ag_3AuS_2 is considered to be due to the unsymmetry of the S-Au-S bond; the fraction of 6s-character is enhanced in the σ-bonding orbital from the viewpoint of energy. The increase in 6s-character leads to a large I.S. value, because the nuclear radius term $\Delta R/R$ is positive in sign for ^{197}Au.

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