I-129 and Au-197 Mössbauer Spectroscopy of AuI and $AgAuI_2$

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Mössbauer spectroscopy of ^{129}I and ^{197}Au nuclei has been applied for AuI and $AgAuI_2$ to clarify the electronic structures of the gold and iodine atoms, and to investigate the nature of the Au-I bonds. In the ^{129}I Mössbauer spectra the sign of e^2qQ is positive for AuI, whereas the sign is negative for $AgAuI_2$. This is attributable to the difference in molecular structures: The iodine atom in AuI is bridged by two gold atoms and in $AgAuI_2$ the iodine is terminal. The ^{197}Au Mössbauer spectra suggest that the Au-I bond in $AgAuI_2$ is more covalent than that in AuI. We have revealed that $AgAuI_2$ consists of Ag^+ and linear $[I\text{-}Au\text{-}I]^-$ units from the Rietveld refinement of the X-ray powder diffraction pattern.

Key words: ^{129}I Mössbauer Spectra; ^{197}Au Mössbauer Spectra; Rietveld Analysis;
Electric Field Gradient; Isomer Shift.

1. Introduction

Iodine compounds have been extensively studied by the nuclear quadrupole resonance (NQR) method, which gives accurate quadrupole coupling constants e^2qQ and asymmetry parameters η. Mössbauer spectroscopy of iodine not only provides such constants, but also the sign of the electric field gradient V_{zz}, the isomer shift δ, and lattice dynamics information. Mössbauer spectroscopic studies are performed with both ^{127}I (100% natural abundance) and ^{129}I (radioactive: $t_{1/2} = 1.6\times10^7$ y) nuclei. The latter nucleus has the advantages of a much smaller line-width and a much higher recoilless fraction, though sample preparations involve difficulty. The ground state of the ^{129}I nucleus has a nuclear spin of 7/2 and a quadrupole moment of –0.55 barn. The 27.8 keV excited state has a spin of 5/2, $Q_{\text{ex}}/Q_{\text{gnd}} = 1.231$, and the half-life of 16.8 ns. The lifetime leads to a natural line-width of 0.29 mm s^{-1}, corresponding to 6.7 MHz. Fortunately, since the quadrupole moment is large, the Mössbauer spectra are usually well resolved.

The ^{197}Au isotope is also observable for both NQR and Mössbauer spectroscopy. The ground state has a nuclear spin of 3/2 and a quadrupole moment of +0.59 barn. The 77.3 keV excited state has a spin of 1/2 and a half-life of 1.88 ns. The latter property leads to a natural line-width of 0.94 mm s^{-1}. Quadrupole-split spectra are simple doublets. From the values of the isomer shift and the quadrupole splitting, gold(I) and gold(III) compounds are easily distinguished. In the present work the Mössbauer spectroscopy of ^{129}I and ^{197}Au nuclei is applied for AuI and $AgAuI_2$ to clarify the electronic structures of the gold and iodine atoms, and to investigate the nature of the Au-I bonds.

AuI consists of zigzag chains of gold and iodine atoms [1]. Gold is linearly coordinated by two iodine atoms at a distance of 2.62 Å, and iodine is bridged by two gold atoms with the angle ∠AuIAu of 72.6°. The small angle can be ascribed to the large polarizability of the iodine atom. Actually, the angle ∠AuClAu for isomorphous AuCl is 92°, larger than 90°. AuBr has two modifications, in which the corresponding angles are 92.3° and 77.1° for the high and low temperature phases, respectively. The former phase is the AuCl type, and the latter the AuI type. In the AuI type the Au-Au distance is shorter than in the AuCl type, suggesting some Au-Au interaction.

A stoichiometric compound $AgAuI_2$ is known to exist in AgI-AuI solid solutions [2]. The compound has three structural modifications. At 55 °C γ-phase transforms into β-phase and at 127 °C β-phase transforms into α-phase. The low temperature modification γ-$AgAuI_2$ is reported to be tetragonal with a = 9.010 Å and c = 6.424 Å from X-ray powder diffraction. Unfortunately, the molecular structure is unknown yet. We have analyzed in detail the observed diffraction pattern by the Rietveld method and elucidated the molecular structure of $AgAuI_2$ consisting of Ag^+ and linear $[I\text{-}Au\text{-}I]^-$ units.

2. Experimental

2.1. Sample Preparation

Radioactive $Au^{129}I$ was prepared as follows. A commercially available $Na^{129}I$ in reductive Na_2SO_3 solution was used in the sample preparation. After oxidizing the iodide with 3 mol dm^{-3} H_2SO_4 and 10% H_2O_2, the resulting molecular iodine was extracted with carbon tetrachloride. The carbon tetrachloride solution was washed thoroughly with water and passed through a Teflon filter to eliminate a slight amount of water. The molecular iodine in carbon tetrachloride was again reduced with a stoichiometric amount of a Na_2SO_3 solution by titration. $Au^{129}I$ was precipitated by adding a large excess of the $Na^{129}I$ solution to an $AuCl_3$ acidic solution. The liberated iodine, which is formed by the reduction of Au(III) to Au(I), was removed in the vacuum line with a chilled trap. $AgAu^{129}I_2$ was prepared by heating equimolar amounts of AgI and $Au^{129}I$ in an evacuated glass tube at 130 °C for 1 week. The samples were identified by X-ray powder diffraction patterns.

The ^{129}Te ($t_{1/2}$ = 70 min) Mössbauer source was prepared by irradiating 150 mg $^{66}Zn^{128}Te$ compound at a thermal neutron fluence rate of 2×10^{13} n cm^{-2} s^{-1} for 1 h in KUR. The 6 mCi source was used for a 3 - 4 h period. The single line $^{66}Zn^{128}Te$ compound (V_{zz} = 0 for zinc-blende structure) was prepared by melting stoichiometric amounts of ^{66}Zn and ^{128}Te in a quartz tube at 1100 °C for 3 h. The ^{197}Pt ($t_{1/2}$ = 18 h) source was also produced by neutron irradiation of a 140 mg ^{196}Pt metal foil in a similar manner as ^{129}Te. The initial activity was 5 mCi.

2.2. Measurement

The Mössbauer measurements were carried out in transmission geometry by cooling the source and the absorber sample to 15 K with a closed cycle helium refrigerator. The absorber thickness was 8 mg $^{129}I/cm^2$ for ^{129}I and 150 mg $^{197}Au/cm^2$ for ^{197}Au measurement. The 27.8 keV γ-ray from ^{129}Te and 77.3 keV γ-ray from ^{197}Pt were detected with 1 mm-thick and 5 mm-thick NaI(Tl) scintillation detectors, respectively. The velocity scales for the spectrometer were calibrated with the well-known α-Fe spectrum at room temperature. X-ray powder diffraction patterns were measured with a Rigaku and a Rad-B system using Cu-Kα radiation. The observed diffraction patterns were analyzed by Rietveld refinement with a Fortran program RIETAN [3].

3. Results and Discussion

3.1. I-129 Mössbauer Spectra

As a result of the interaction of the electric field gradient (EFG) with the nuclear quadrupole moment, the nuclear ground state ($I = 7/2$) and the excited state ($I^* = 5/2$) split into 4 and 3 sublevels, respectively. Since the γ-transition is the magnetic dipole (M1) transition, $\Delta m = 0$ and $\Delta m = \pm1$ transitions are allowed. Then, eight transitions occur for a small η value, as shown in Figure 1. The transition probabilities are proportional to the square of the Clebsh-Gordan coefficients for the polycrystalline sample. The ^{129}I Mössbauer spectra of AuI and $AgAuI_2$ at 15 K are shown in Figure 2. In the AuI spectrum

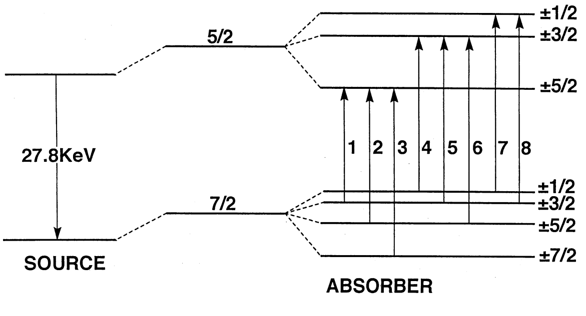

Fig. 1. Energy levels of ^{129}I. The quadrupole splitting of the absorber levels corresponds to positive electric field gradient ($V_{zz} > 0$).

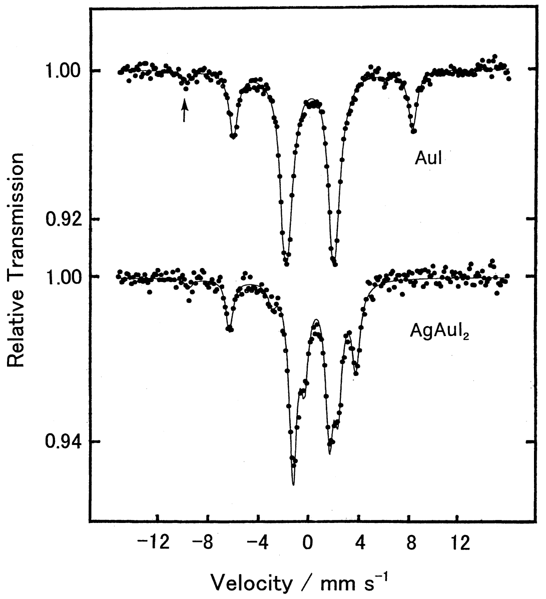

Fig. 2. ^{129}I Mössbauer spectra of AuI and $AgAuI_2$ at 15 K. The arrow in AuI shows the forbidden transition, corresponding to $I_{ex} = 1/2 \rightarrow I_{gnd} = 5/2$.

a "forbidden" transition line is recognized at about −10 mm s^{-1}. Such a line originates from the mixing of two sublevels having m values differed by ±2, when the asymmetry parameter is large. From the positions of the lines, the quadrupole coupling constant (magnitude and sign), the asymmetry parameter η, and the isomer shift δ were derived using the relation

$$E_{ij} = A[Rf(I^*, m_i^*, \eta) - f(I, m_j, \eta)] + \delta, \quad (1)$$

where $A = e^2qQ/4$, $f(I, m, \eta)$ is related to the spin Hamiltonian eigenvalues for the case of non-axial symmetric electric field, and R is the quadrupole moment ratio of ^{129}I (= Q^*/Q = 1.232). The values of $f(I, m, \eta)$ were numerically calculated by Cohen for intervals of 0.1 in η [4]. Using these values, the line positions E_{ij} have been calculated as functions of e^2qQ, η, and δ by Pasternak and Bukshpan [5]. Table 1 gives the experimental values of the isomer shift with respect to the ZnTe source, e^2qQ (magnitude and sign), and η, obtained from the line positions of the best-fitted spectra. The e^2qQ values converted to ^{127}I, using the ratio $e^2q^{127}Q/e^2q^{129}Q = 1.426$, are given in parentheses.

Table 1. Mössbauer parameters of ^{129}I and ^{197}Au for AuI and $AgAuI_2$.

	^{129}I			^{197}Au	
	δ^a (mm/s)	e^2qQ (MHz)	η (%)	δ^b (mm/s)	2ε (mm/s)
AuI	0.17	+669 (^{127}I +954)	69	−1.23 (−1.26)^c (−1.32)^d	3.95 (3.94)^c (3.98)^d
$AgAuI_2$	0.08	−532 (^{127}I −759)	25	−0.50	4.49

[a] The isomer shifts are relative to the ZnTe source. [b] The isomer shifts are relative to the Pt source. [c] H. D. Bartunik et al., Z. Physik **240**, 1 (1970). [d] M. O. Faltens and A. D. Shirley, J. Chem. Phys. **53**, 4249 (1970).

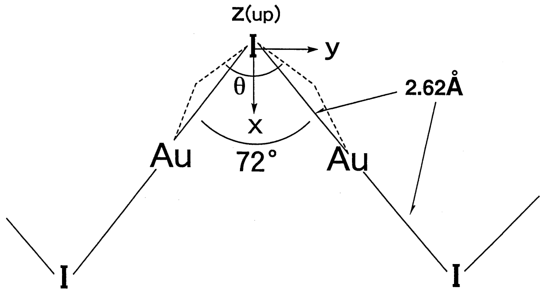

Fig. 3. Bonding scheme and directions of the principal axes of AuI.

It is interesting that the sign of e^2qQ for AuI is positive (i. e., V_{zz} is negative), whereas the sign is negative for $AgAuI_2$ (positive V_{zz}). This experimental fact might be due to the difference in molecular structures: The iodine atom in AuI is bridged by two gold atoms and in $AgAuI_2$ the iodine is terminated. It is reasonable to choose for the former that the principal z-axis of the EFG is perpendicular to the direction of the Au-I bond, i. e., to the plane including Au-I-Au, as shown in Figure 3. In this case the components of the field gradient tensors are given, using the angle θ for ∠AuIAu, as follows:

$$\begin{aligned} V_{xx} &= (1 - 3\cos\theta)eq/4, \\ V_{yy} &= (1 + 3\cos\theta)eq/4, \qquad (2) \\ V_{zz} &= -eq/2, \end{aligned}$$

and $V_{xy} = V_{yz} = V_{zx} = 0$. The asymmetry parameter is defined as

$$\eta \equiv |V_{xx} - V_{yy}|/V_{zz} = -3\cos\theta. \quad (3)$$

From (3) the observed η value gives an angle θ of 103°, which is considerably large than that of the

X-ray structural analysis (72.6°). The discrepancy is interpreted as follows: In the X-ray structural analysis each atom is situated in a position having the highest total electron density (essentially core electrons), whereas the EFG tensor gives the direction of the bonding orbital made of the bonding electrons (mainly 5p-electrons). On the other hand, in the $AgAuI_2$ compound the principal z-axis of the EFG may be parallel to the Au-I bond axis. Due to our structural analysis of $AgAuI_2$, the iodine atom exists as a linear $[I\text{-}Au\text{-}I]^-$ ion and interacts weakly with Ag^+, as mentioned below. The interaction may induce a non-zero η value.

The EFG and the asymmetry parameter are directly related to the electronic distribution in the molecule. According to Townes and Dailey's approximation, one may express the observed e^2qQ_{obs} in the following way:

$$U_{\text{p}} = e^2qQ_{\text{obs.}}/e^2qQ_{\text{at.}} = (N_x+N_y)/2-N_z, \quad (4)$$

where U_{p} is the number of unbalanced p electrons, $e^2qQ_{\text{at.}}$ is the atomic quadrupole coupling constant (–2292.7 MHz for ^{127}I), and N_x, N_y, and N_z are the number of p-electrons along the x, y and z axes, respectively. The asymmetry parameter is given as

$$\eta = 3(N_x - N_y)/2U_{\text{p}}. \quad (5)$$

On the other hand, the isomer shift, which is unique to Mössbauer spectroscopy, is related to the electronic density in the molecule. According to Bukshpan et al. [6], the isomer shift δ relative to the ZnTe source is experimentally given by

$$\delta = -9.2h_{\text{s}} + 1.5h_{\text{p}} - 0.54\,(\text{mm s}^{-1}), \quad (6)$$

where h_{s} and h_{p} are the number of holes in the 5s and 5p shell, respectively. The s and p holes are related to the s- and p-electron populations by

$$h_{\text{s}} = 2 - N_s,\ h_p = 6 - (N_x + N_y + N_z). \quad (7)$$

Table 2. Electron populations of $5p_x$, $5p_y$, and $5p_z$ orbitals and the numbers of unbalanced p electrons, 5p holes, and 5s holes.

	N_x	N_y	N_z	U_{p}	h_{p}	h_{s}
AuI	1.68	1.49	2.00	–0.42	0.83	0.06
$AgAuI_2$	2.00	1.95	1.64	0.33	0.41	0.00

In the case of AuI since the p_z-orbital electrons along the principal z-axis do not take part in Au-I bond formation, they would remain as a non-bonding pair, i. e., N_z = 2.00. Substituting the observed values of e^2qQ_{obs} and η into (4) and (5), one obtains N_x = 1.68 and N_y =1.49. Therefore, the total number of p holes h_{p} is calculated to be 0.83 from (7). Inserting the values of δ and h_{p} into (6), we obtained h_{s} = 0.06, corresponding to 6.7% s-character $\{= 100\,h_{\text{s}}/(h_{\text{s}} + h_{\text{p}})\}$ of the iodine bond. This sp hybridization would be consistent with the bond angle of 103°, larger than 90°. The iodine configuration in AuI is obtained to be $5s^{1.94}5p^{5.17}$. It is concluded that 0.11 e^- is transferred from the two gold atoms to the $5p_x$ and $5p_y$ orbitals of iodine. In the case of $AgAuI_2$ it is reasonable to assume no s-character in the iodine bond. When the experimental values of e^2qQ_{obs}, η and δ are substituted in (4) - (7), we obtain N_x = 2.00, N_y = 1.95 and N_z = 1.64, as given in Table 2. The results suggest that two π orbitals, p_x- and p_y-orbitals, are lone pairs and do not take part in the $[I\text{-}Au\text{-}I]^-$ bond formation, although the p_y-orbital interacts weakly with a Ag^+ ion, donating 0.05 e^- of the p_y-orbital to the 5s orbital of the Ag^+ ion. The iodine configuration in $AgAuI_2$ is also obtained to be $5s^{2.00}5p^{5.59}$. It is interesting to compare this result with a linear, symmetric $[I\text{-}I\text{-}I]^-$ ion. The Mössbauer data of the I_3^- ion indicated that the central iodine atom has a slightly positive charge, and two terminal iodine atoms have a negative charge of 0.5 [7]. That is, the ionic charge is localized on the terminal atoms. Therefore it is reasonable to assign the ionic charge of $[I\text{-}Au\text{-}I]^-$ to two terminal iodine atoms. Under this condition we find that 0.14 e^- is transferred from the gold atom to the $5p_z$ orbital of iodine, due to the difference in the electronegativities of the Au and I atoms.

3.2. Au-197 Mössbauer Spectra

Figure 4 shows the ^{197}Au Mössbauer spectra of AuI and $AgAuI_2$ at 15K, which consist of the simple quadrupole doublets. The $AgAuI_2$ spectrum indicates the existence of small amounts of gold metal impurities. These spectra were fitted with Lorentzian curves by the least-squares method. The isomer shift (δ) relative to the Pt source and the quadrupole splitting of the ground state $\left\{2\varepsilon = \frac{1}{2}e^2qQ(1+\eta^2/3)^{1/2}\right\}$ are given in Table 1. Because of the quadrupole doublet with an equal line intensity for the polycrystalline sample, the sign of V_{zz} cannot be experimentally determined.

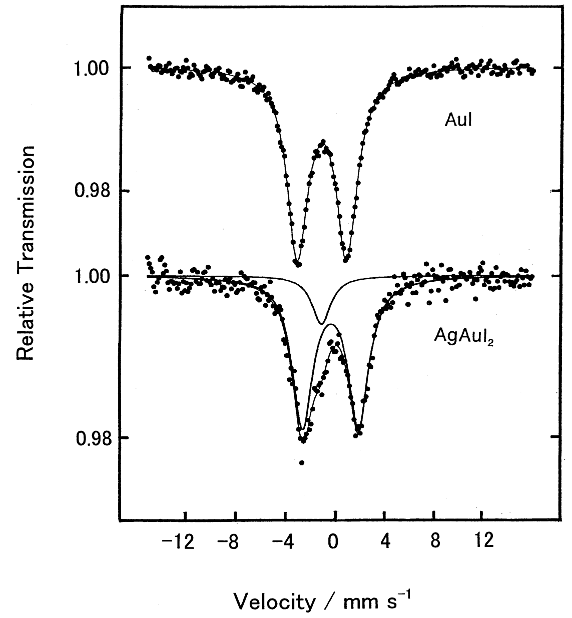

Fig. 4. ^{197}Au Mössbauer spectra of AuI and $AgAuI_2$ at 15 K. The spectrum of $AgAuI_2$ indicates the existence of gold metal impurities.

However, it is reasonable to assume that the electronic configuration of Au(I) linearly coordinated with two ligands (L) is approximately written as $5d^{10}(6s6p_z)^N$, as pointed out by Faltens and Shirley [8]. If the L-Au-L bond is perfectly covalent, the gold atom would have one 6s and one $6p_z$ electrons ($N = 1$). The $6p_z$ electron will negatively contribute to V_{zz}. On the contrary, if the bond is perfectly ionic, this leads to a closed shell $5d^{10}$ configuration that does not give rise to V_{zz} ($N = 0$). The sign of V_{zz} in $KAu(CN)_2$, consisting a linear $[CN\text{-}Au\text{-}CN]^-$ ion, is experimentally established to be negative [9]. Therefore, we shall assume the sign of V_{zz} is negative for both AuI and $AgAuI_2$. Since the quadrupole splitting of $AgAuI_2$ is smaller than that of AuI, the Au-I bond in $AgAuI_2$ is more covalent than that in AuI, because the increase in the covalent character of the L-Au-L bond leads to a decrease in magnitude of V_{zz}. On the other hand, the isomer shift is proportional to the s-electron density on the gold atom [8]. The increase in the covalent character, i. e., increase in the quantity N, induces the increase in 6s electrons in the bonding. Since the isomer shift of $AgAuI_2$ is larger than of AuI, the Au-I bond in $AgAuI_2$ is more covalent than that in AuI. That is, from the both values of the quadrupole splitting and the isomer shift it is confirmed that the Au-I bond in $AgAuI_2$ is more covalent than that in AuI. These results suggest that the Au-I bond length in $AgAuI_2$ is shorter than in AuI, in good agreement with the result of the Rietveld analysis of $AgAuI_2$.

3.3. Rietveld Refinement of $AgAuI_2$

X-ray diffraction powder pattern of $AgAuI_2$ is shown in Figure 5. The compound was confirmed to be tetragonal with space group $P4_2/mbc$ by our Rietveld refinement. The final refinement is depicted with solid lines in Figure 5. The crystallographic data and experimental details, and the atomic positions and the thermal parameters are given in Tables 3 and 4, respectively. Figure 6 shows the crystal structure of $AgAuI_2$, consisting of Ag^+ and a linear, symmetric $[I\text{-}Au\text{-}I]^-$ ion. The Au-I bond distance is estimated to be 2.57 Å, close to the Au-I bond of the free $AuI_2{}^-$ ion (2.561 Å) [10], which is shorter than that of AuI (2.62 Å). This suggests that the Au-I bond in $AgAuI_2$ is more covalent than that in AuI, consistent with the results of the ^{197}Au Mössbauer spectra. The

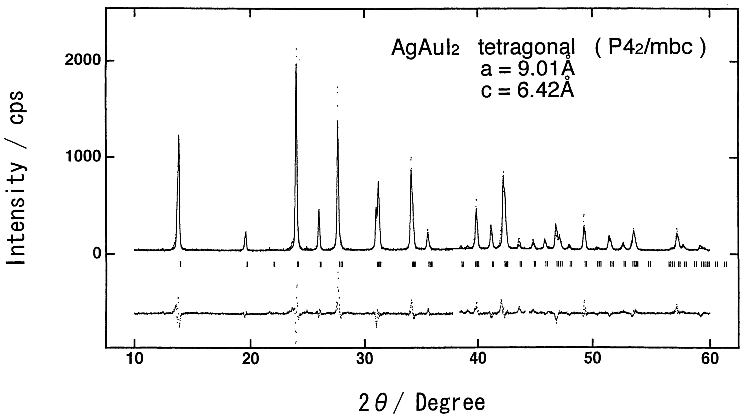

Fig. 5. X-ray powder diffraction pattern of γ-$AgAuI_2$ at 294 K. The solid lines indicate final Rietveld refinement.

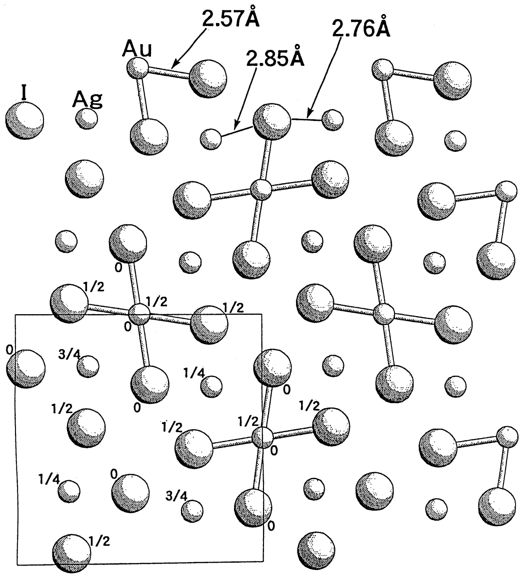

Fig. 6. Crystal structure of γ-$AgAuI_2$ at 294K. γ-$AgAuI_2$ consists of Ag^+ and linear, symmetric $[I\text{-}Au\text{-}I]^-$ ions.

$Ag^+ \cdots I$ interaction is observed at a distance of 2.76 Å, which is the reason of the large asymmetry parameter (η = 0.25) of iodine.

Table 3. Crystal data and experimental details of Rietveld Refinements for $AgAuI_2$.

Phase	γ
Temperature / K	294
Crystal system	tetragonal
Space group	$P4_2/mbc$
Lattice constants	a = 9.013(1), c = 6.426(1) Å
d_{calc} / g cm^{-3}	7.108
Z	2
Number of parameters	28
2θ / °	10 - 60
Step width / °	0.02
R_P[a]	0.122
R_F[b]	0.061
DS, RS, SS / °[c]	0.5, 0.15, 0.5

[a] $R_P = \Sigma \left| y_i(\text{obs}) - y_i(\text{cal}) \right| / \Sigma y_i(\text{obs})$, where $y_i(\text{obs})$ and $y_i(\text{cal})$ are the observed and calculated intensity at ith step. [b] $R_F = \Sigma \left| (I_k(\text{obs})^{1/2} - (I_k(\text{cal})^{1/2} \right| / \Sigma I_k(\text{obs})^{1/2}$, where I_k is the intensity assigned to the kth Bragg reflection. [c] Divergence slit, receiving slit, and scatter slit.

Table 4. Positional and thermal parameters of $AgAuI_2$ (phase γ, space group $P4_2/mbc$) with estimated standard deviations in parentheses.

Atom	Position	Occupation	x	y	z	B_{iso}/Å^2
Ag	8g, 2	0.5	0.294(4)	x + 0.5	0.25	16.5(26)[a]
Au	4c, 2/m	1	0	0.5	0	3.4(8)
I	8h, m	1	0.214(2)	0.041(2)	0	3.3(10)

[a] The isotropic thermal parameter was calculated from the anisotropic parameters β_{11} = 0.027(32), β_{22} = 0.010(15), β_{33} = 0.226(61), β_{12} = 0.008(15), β_{13} = –0.060(15), and β_{23} = –0.011(25).

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