# Analysis of $^{109}$Ag MAS NMR Chemical Shieldings Observed in $Ag_xCu_{1-x}I$ Crystals

Tomonori Ida, Kazunaka Endo,[*] Masahiko Suhara, Motoko Kenmotsu,[†] Kenji Honda,[††]

Susumu Kitagawa,[††] and Hiroyuki Kawabe[†††]

Department of Chemistry, Faculty of Science, Kanazawa University, Kakumamachi, Kanazawa 920-1192

[†]Tsukuba Research Laboratory, Mitsubishi Paper Mills, Ltd., 46 Wadai, Tsukuba 300-4247

[††]Department of Industrial Chemistry and Biochemistry, Faculty of Engineering, Kyoto University, Kyoto 606-8501

[†††]Secretarial Department, Kinjo College, Matto 924-8511

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$^{109}$Ag NMR signals in $Ag_xCu_{1-x}I$ crystals were shifted to a low field relative to that in solid AgI with decreasing the unit cell constant analogously to $^{63}$Cu MAS NMR signals reported in a previous study. The observed chemical shieldings were analysed using the results of Ag and Cu NMR shielding calculations of tetrahedral ($T_d$) $MI_4^{3-}$ (M = Ag, Cu) complex ions with the ab initio GAUSSIAN 94 program using a double-$\zeta$ basis set for the Ag, Cu, and I atoms. Since the shift is explained dominantly by the paramagnetic shielding term, which depends on the d-hole and p-electron densities in Ag or Cu atoms for the $MI_4^{3-}$ complex ions, the observed $^{109}$Ag shift moved to a low field with decreasing the lattice constant, corresponding to an increase in the d-hole and p-electron densities for $AgI_4^{3-}$ ($R_{Ag-I}$ = 2.68, 2.73, 2.77 Å) relative to the $AgI_4^{3-}$ ($R_{Ag-I}$ = 2.81 Å) ion.

Experimental and theoretical studies on the NMR properties in metal complexes contain a lot of valuable information concerning the nature of the chemical bonds between metals and ligands. Studies of the magnetic properties provide information about the roles of the electrons of higher angular momentum in these chemical bonds. We performed both theoretical and experimental studies[1—3] on the metal NMR chemical shifts in Ag, Cd, Cu, and Zn complexes in solution using ab initio MO calculations of isolated metal complexes. In previous studies,[2,3] we considered the relation between the metal chemical shift and the coordination number in solution.

For a solid AgI of zincblende structure, Becker and co-worker[4] observed the $^{109}$Ag signal of the tetrahedral ($T_d$) AgI at 800—740 ppm relative to a 9.0 M AgNO$_3$ aqueous solution (1 M = 1 mol dm$^{-3}$) in the temperature range of 300—420 K. We also indicated that the $^{109}$Ag signal of the $AgI_4^{3-}$ ion in aqueous solution is observed at 739 ppm relative to a 1.0 M AgNO$_3$ solution.[2] The Ag chemical shielding of the silver complex in solution is in considerably good accordance with that in a solid, as obtained in organic compounds that the nuclear chemical shieldings in solution correspond well to the shieldings in a solid. We, accordingly, expect that experimental metal NMR chemical shieldings of solid metal iodides can be analysed using the metal chemical shielding in isolated metal iodide $MI_4^{3-}$ (M = Ag, Cu) ions calculated by ab initio MO programs.

In a previous study,[5] although the $^{63}$Cu MAS NMR signals in $Ag_xCu_{1-x}I$ crystals were shifted to a low field relative to $Ag_{0.75}Cu_{0.25}I$ with decreasing the lattice constant, we didn't

indicate the theoretical reason. This study aimed to clarify the theoretical reason for the low field shifts and the roles of the electrons in the chemical bonds of Ag- and Cu-iodide complexes. In the present paper, we describe that $^{109}$Ag low-field shifts in $Ag_xCu_{1-x}I$ relative to solid AgI are in proportion to the decrease of the lattice constant of the complete solid solution. We will explain the observed shifts by Ag and Cu chemical shieldings in $MI_4^{3-}$ (M = Ag, Cu) complex ions calculated by applying a finite perturbation method using an ab initio GAUSSIAN 94 program[6] with a double-$\zeta$ basis set.[7]

## Experimental

We measured the $^{109}$Ag MAS NMR spectra at a frequency of 12.45 MHz, using a JEOL GX-270 spectrometer. 120 Transients were accumulated using an 8.5 μs (90°) pulse. The spectra were obtained under magic-angle spinning at a speed of about 5 kHz; 8 k data points were collected over band widths of 20 kHz. All measurements were carried out at 300 K and solid AgI was used as an external reference.

Crystalline $Ag_xCu_{1-x}I$ in which the solid solution was complete was prepared by a melt annealing method in a vacuum vessel to prevent oxidation. The Ag/Cu for mixed crystals was estimated using an X-ray fluorescence method.

The X-ray diffraction profiles of the $Ag_xCu_{1-x}I$ (x = 0.25, 0.50, 0.75) crystal shown in Fig. 1 indicate a cubic zincblende structure, and the lattice parameter changes linearly with the Ag or Cu concentration with no change in the crystal structure. Since the unit-cell dimension given in Fig. 2 follows well the Vegard law,[8] $Ag_xCu_{1-x}I$ crystals are expected to form a complete solid-solution.

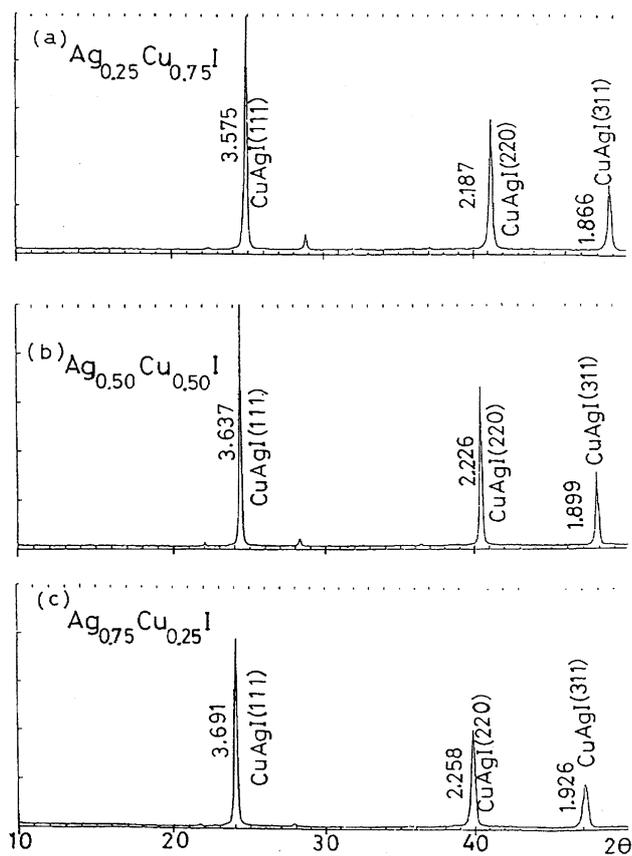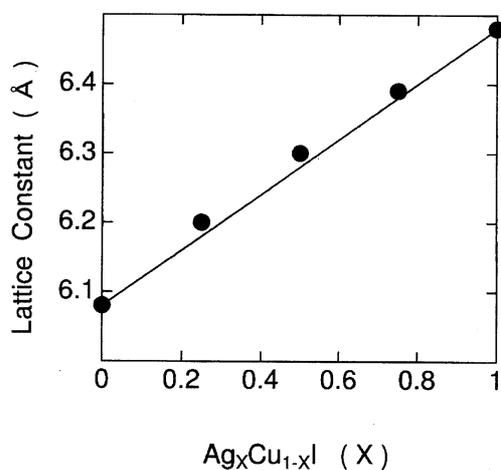Fig. 1.   X-Ray diffraction profiles of $Ag_xCu_{1-x}I$ crystal for $x = 0.25, 0.5,$ and 0.75.



Fig. 2.   The unit cell dimension of $Ag_xCu_{1-x}I$ crystal versus $x = 0.0, 0.25, 0.50, 0.75,$ and 1.0; The solid line is the Vegard law.

**Computation.**   As the structural data of tetrahedral $AgI_4^{3-}$ and $CuI_4^{3-}$ complex ions in the $\gamma$-phase, we used the lattice constants of $Ag_xCu_{1-x}I$ crystals determined in our X-ray diffraction measurements. The coordinations in $MI_4^{3-}$ (M = Ag, or Cu) ions were estimated as M(0, 0, 0), I($-c/4$, $-c/4$, $-c/4$), I($-c/4$, $c/4$, $c/4$), I($c/4$, $-c/4$, $c/4$), I($c/4$, $c/4$, $-c/4$), where $c$ denotes the lattice constant in the $\gamma$-phase. We used $c$ of the unit lattice constants as (6.20, 6.30, 6.39, and 6.48 Å) for a $T_d$ $AgI_4^{3-}$ complex ion, and (6.08, 6.20, 6.30, and 6.39 Å) for a $T_d$ $CuI_4^{3-}$ ion, respectively. Ag

and Cu chemical shielding constants were calculated by the finite-perturbation method using the GAUSSIAN 94 program[6] using a double-$\zeta$ basis set[7] for the Ag, Cu, and I atoms. Then, ab initio MO calculations were performed on a DEC VT-Alpha 533 workstation.

## Results and Discussion

We obtained complete solid solution $Ag_xCu_{1-x}I$ crystals in a zincblende structure, as indicated by the X-ray diffraction measurement. The $^{109}$Ag MAS NMR signals of the $Ag_xCu_{1-x}I$ crystals, shown in Fig. 3 and Table 1, were seen to shift with broadening to a low field relative to AgI. We emphasise that the low-field shifts of the Ag and Cu signals were observed linearly with decreasing the lattice constant of the mixed crystals shown in Table 1. We were interested in experimental and theoretical studies[1-3] on the chemical shifts of metal NMR for metal complexes in solution and a solid. We will explain the metal low field shift with decreasing the lattice constant by the ab initio MO calculations of isolated $MI_4^{3-}$ (M = Ag, Cu) complex ions. The bond length, $R_{Ag,Cu-I}$, in $MI_4^{3-}$ (M = Ag, Cu) was calculated from the unit lattice constants of $Ag_xCu_{1-x}I$ (x = 0.0, 0.25, 0.50, 0.75, 1.0) given in Table 1.

In Table 2, we have summarized the Ag and Cu nuclear shielding constants and chemical shifts in $MI_4^{3-}$ (M = Ag, Cu) with the observed chemical shifts in $Ag_xCu_{1-x}I$ crystals (x = 0.0, 0.25, 0.50, 0.75, 1.0). The calculated Ag and Cu shifts are given relative to the reference molecules, $AgI_4^{3-}$ ($R_{Ag-I} = 2.81$ Å) and $CuI_4^{3-}$ ($R_{Cu-I} = 2.77$ Å), respectively. In the table, we give the observed Ag and Cu shifts of $Ag_xCu_{1-x}I$ relative to the AgI and $Ag_{0.75}Cu_{0.25}I$, respectively. The calculated Ag and Cu chemical shieldings in
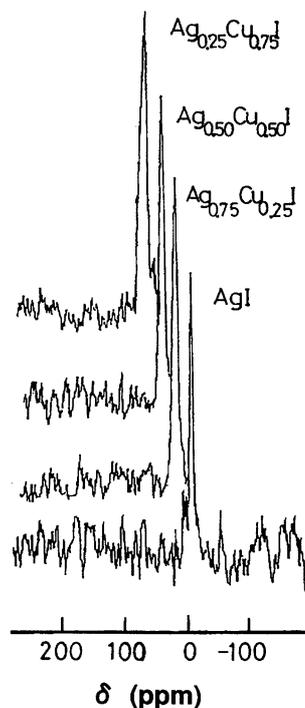


Fig. 3.   $^{109}$Ag MAS NMR spectra of $Ag_xCu_{1-x}I$ crystal for $x = 0.25, 0.5, 0.75,$ and 1.0.

Table 1.   Observed Ag and Cu Chemical Shifts, Half-Linewidths, and Unit Lattice Constants of $Ag_xCu_{1-x}I$ Crystal

|  |  | $Ag_xCu_{1-x}I$ crystal | | | |
|---|---|---|---|---|---|
|  | CuI | $Ag_{0.25}Cu_{0.75}I$ | $Ag_{0.5}Cu_{0.5}I$ | $Ag_{0.75}Cu_{0.25}I$ | AgI |
| Ag chemical shift (ppm) |  | 72.6 | 43.1 | 28.0 | 0.0 |
| Ag half-linewidth (Hz) |  | 200 | 120 | 120 | 85 |
| Cu chemical shift (ppm) | 32.9 | 18.8 | 6.0 | 0.0 |  |
| Cu half-linewidth (Hz) | 256 | 1608 | 1805 | 1427 |  |
| Unit lattice constant (Å) | 6.08 | 6.20 | 6.30 | 6.39 | 6.48 |

Table 2.   Calculated Ag and Cu Chemical Shielding Constants and the Shifts of $T_d$ $AgI_4^{3-}$ and $T_d$ $CuI_4^{3-}$ Complex Ions, Respectively with Observed Chemical Shifts of $Ag_xCu_{1-x}I$ Crystal

| $MI_4^{3-}$ Complex | Calculated shielding constant | | | Shift | $Ag_xCu_{1-x}I$ | Observed shifts |
|---|---|---|---|---|---|---|
| $R_{M-I}$ | $\sigma_{dia}$ | $\sigma_{para}$ | $\sigma_{total}$ |  |  |  |
| Å | ppm | ppm | ppm | ppm |  | ppm |
| Ag shielding constant | | | | | | |
| $AgI_4^{3-}$ (2.81) | 4679 | −1272 | 3407 | 0 | AgI | 0.0 |
| $AgI_4^{3-}$ (2.77) | 4679 | −1370 | 3309 | 98 | $Ag_{0.75}Cu_{0.25}I$ | 28.0 |
| $AgI_4^{3-}$ (2.73) | 4680 | −1472 | 3208 | 199 | $Ag_{0.50}Cu_{0.50}I$ | 43.1 |
| $AgI_4^{3-}$ (2.68) | 4680 | −1588 | 3092 | 315 | $Ag_{0.25}Cu_{0.75}I$ | 72.6 |
| Cu shielding constant | | | | | | |
| $CuI_4^{3-}$ (2.77) | 2406 | −695 | 1711 | 0 | $Ag_{0.75}Cu_{0.25}I$ | 0.0 |
| $CuI_4^{3-}$ (2.73) | 2406 | −744 | 1662 | 49 | $Ag_{0.50}Cu_{0.50}I$ | 6.0 |
| $CuI_4^{3-}$ (2.68) | 2406 | −806 | 1600 | 111 | $Ag_{0.25}Cu_{0.75}I$ | 18.8 |
| $CuI_4^{3-}$ (2.63) | 2406 | −878 | 1528 | 183 | CuI | 32.9 |

$MI_4^{3-}$ (M = Ag, Cu) are dominated by the paramagnetic term, since the diamagnetic terms are constant ($\sigma_{dia}$ = 4679—4680, and 2406 ppm for $AgI_4^{3-}$ and $CuI_4^{3-}$, respectively). For both metal complexes, the calculated shifts reflect the observed qualitative trends well to the low field.

Let's consider the reason why the calculated values of the isolated complex ions are not in quantitative agreement with the observed ones. The calculated shieldings of isolated $MI_4^{3-}$ seem to be overestimated in comparison with the observed shifts in solid $Ag_xCu_{1-x}I$, because the electron donations from iodines to metal ions, and back donations to iodines from d-electron of metal ions due to repetitive ion structures in solid, become considerably less than those in the isolated complex ions. We expect that the results reflect the paramagnetic terms dominantly. A more quantitative accordance may be obtained at least by performing ab initio MO calculations of the $MI_4^{3-}$ ion, including the nearest-neighbor $MI_4^{3-}$ complex ions. On the other hand, we didn't consider a theory for the chemical shift in which spin-orbit coupling is introduced through perturbation theory.[9−11] The spin-orbit shift, as derived by third-order perturbation theory, comes from a cross term involving the external field-orbit interaction, the halogen spin-orbit and Fermi's contact interaction. In the $SiX_4$ molecule, a [29]Si high field shift of $SiI_4$ could be explained by a spin-orbit effect on the shifts of the molecules containing heavy halogen atoms.[10] Since the effects are more positive for the metal shielding constant with decreasing the bond length, $R_{M-I}$, of $MI_4^{3-}$, the total shifts approximate the observed values.

In order to clarify the theoretical reason for the low field shifts and the roles of the electrons in the chemical bonds of Ag- and Cu-iodide complexes, we examined the change in the valence atomic orbital (AO) densities of the Ag and Cu ions and I in $MI_4^{3-}$ (M = Ag, Cu). The results are given in Table 3. In this table, the total density increases in the $ns$ and $np$ AOs of Ag ($n$ = 5) and Cu ($n$ = 4) atoms and the density decreases in the s and p AOs of iodine atoms indicate electron transfers from the iodines to metal atoms. Back donations to iodines also produce holes in the $(n-1)$d orbitals of Ag ($n$ = 5) and Cu ($n$ = 4) atoms due to $d\pi$(metal)−$p\pi$(ligand) interaction of metal iodide complexes. It is interesting that the metal chemical shielding constants depend on the electron and hole density increases in the valence s, p, and d orbitals of metal atoms with decreasing the bond length between metal and iodine atoms.

As reported earlier for solution [109]Ag and [63]Cu NMR studies,[2,3] the chemical shieldings of silver- and copper-iodide complexes can be governed by the paramagnetic term. This will be explained by the following equation for [109]Ag and [63]Cu chemical shieldings:

$$\sigma_{para} = \left(\frac{-2\alpha^2}{3}\right)\left[\left(\frac{\langle 1/r^3\rangle_p P_T^e}{E_p}\right) + \left(\frac{\langle 1/r^3\rangle_d 3D_T^h}{E_d}\right)\right], \quad (1)$$

where $P_T^e$ and $D_T^h$ are the total populations of the p electrons and d holes respectively.

Table 3. The Change[a] in Total AO Densities of $T_d$ $AgI_4^{3-}$ and $T_d$ $CuI_4^{3-}$ Complex Ions

| Orbital $R_{M-I}$ = | $MI_4^{3-}$ 2.81 Å | $MI_4^{3-}$ 2.77 Å | $MI_4^{3-}$ 2.73 Å | $MI_4^{3-}$ 2.68 Å | $MI_4^{3-}$ 2.63 Å |
|---|---|---|---|---|---|
| $AgI_4^{3-}$ complex | | | | | |
| Silver | | | | | |
| 4d | −0.0480 | −0.0738 | −0.1014 | −0.1343 | |
| 5s | 0.0905 | 0.1022 | 0.1137 | 0.1262 | |
| 5p | 0.2679 | 0.2824 | 0.2977 | 0.3160 | |
| Iodine | | | | | |
| 5s | −0.0418 | −0.0474 | −0.0530 | −0.0591 | |
| 5p | −0.0529 | −0.0523 | −0.0514 | −0.0503 | |
| $CuI_4^{3-}$ complex | | | | | |
| Copper | | | | | |
| 3d | | −0.0672 | −0.0854 | −0.1098 | −0.1406 |
| 4s | | 0.1423 | 0.1524 | 0.1654 | 0.1810 |
| 4p | | 0.2917 | 0.3132 | 0.3422 | 0.3789 |
| Iodine | | | | | |
| 5s | | −0.0268 | −0.0331 | −0.0411 | −0.0508 |
| 5p | | −0.0760 | −0.0781 | −0.0807 | −0.0841 |

a) The change of the density was evaluated relative to densities of each atomic orbital in the neutral atom.

The contributions to the paramagnetic term for Ag and Cu shieldings can be estimated from $E_{p,d}$ and $\langle 1/r^3 \rangle_{p,d}$ as parameters in Eq. 1. We assume that $E_p \simeq E_d$, $\langle 1/r^3 \rangle_{np}$ = 1.38 or 0.59 a.u. and $\langle 1/r^3 \rangle_{(n-1)d}$ = 3.67 or 5.00 a.u. for Ag ($n = 5$) or Cu ($n = 4$), respectively. (The terms were obtained from the SCF functions by Clementi and co-workers.[9]) Thus, we showed the contributions to the paramagnetic shielding constants of the Cu and Ag for $T_d$ $MI_4^{3-}$ (M = Cu, Ag) complexes in Table 4. From this table, we can see that for Ag complexes the p and d contributions are relatively close and competitive, and for the Cu complexes the d contributions are larger than the p contributions.

## Conclusion

In this paper, we have reported on the experimental results

on metal NMR chemical shieldings in solid metal iodides and the metal chemical shielding calculations in isolated metal iodide $MI_4^{3-}$ (M = Ag, Cu) ions using ab initio MO programs. The results of the ab initio calculations were comparable with the experimental chemical shifts. In $Ag_xCu_{1-x}I$ crystals, we observed cubic lattice constants and $^{109}$Ag NMR chemical shifts linearly dependent on $x$. The observed chemical shieldings were analysed based on the Ag and Cu NMR shielding calculations of tetrahedral $MI_4^{3-}$ (M = Ag, Cu) ions using the ab initio GAUSSIAN 94 program with a double-$\zeta$ basis set for the Ag, Cu, and I atoms. The shift was explained dominantly based on the paramagnetic shielding term, which depends on the d-hole and p-electron densities of the Ag or Cu atom in $MI_4^{3-}$ ions. The observed $^{109}$Ag low field shifts with decreasing the lattice constant correspond to the increase in the d-hole and p-electron densities for the

Table 4. Contributions to the Paramagnetic Term of the Ag and Cu Shielding Constants from the Valence d and p AO for $T_d$ $MI_4^{3-}$ Complex Ions

| Orbital $R_{M-I}$ = | $MI_4^{3-}$ 2.81 Å | $MI_4^{3-}$ 2.77 Å | $MI_4^{3-}$ 2.73 Å | $MI_4^{3-}$ 2.68 Å | $MI_4^{3-}$ 2.63 Å |
|---|---|---|---|---|---|
| $AgI_4^{3-}$ complex | | | | | |
| 4d-Contribution | | | | | |
| ( $2\alpha^2/3E_d$ ) unit | −0.530 | −0.811 | −1.118 | −1.479 | |
| 5p-Contribution | | | | | |
| ( $2\alpha^2/3E_p$ ) unit | −0.370 | −0.390 | −0.411 | −0.436 | |
| $CuI_4^{3-}$ complex | | | | | |
| 3d-Contribution | | | | | |
| ( $2\alpha^2/3E_d$ ) unit | | −1.007 | −1.281 | −1.647 | −2.111 |
| 4p-Contribution | | | | | |
| ( $2\alpha^2/3E_p$ ) unit | | −0.172 | −0.185 | −0.202 | −0.224 |

$AgI_4^{3-}$ ($R_{Ag-I}$ = 2.68, 2.73, 2.77 Å) relative to the $AgI_4^{3-}$ ($R_{Ag-I}$ = 2.81 Å) complex ions.

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