

# Mobility of Silver Ions in Silver Ion Conductor $\text{Ag}_7\text{NbS}_6$ Studied by Ag and Nb NMR

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Temperature dependences of the  $^{109}\text{Ag}$  chemical shift and the spin–lattice relaxation time,  $T_1$ , of  $^{109}\text{Ag}$ ,  $^{107}\text{Ag}$ , and  $^{93}\text{Nb}$  NMR have been measured in the room-temperature phase of  $\text{Ag}_7\text{NbS}_6$  and related compounds. The  $^{109}\text{Ag}$  chemical shift is about 1300 ppm and is much larger than those of other silver compounds. The  $^{109}\text{Ag}$  and  $^{107}\text{Ag}$  line widths are about 200 Hz, and these indicate that the motional narrowing of silver ions has been completed in this phase.  $T_1$  of all nuclei increases with increasing temperature. The relaxation process is explainable by the fluctuations of scalar coupling between silver nuclei, because the  $T_1$  of  $^{109}\text{Ag}$  does not show any magnetic field dependence. The temperature dependences of  $T_1$  of the mobile  $^{109}\text{Ag}$  and  $^{107}\text{Ag}$  are weaker than that of  $T_1$  of the immobile  $^{93}\text{Nb}$  as well found in the case of  $\text{Ag}_9\text{GaSe}_6$ . Though  $\text{Ag}_7\text{NbS}_6$  and related compounds show a high ionic conductivity of  $0.1\text{--}1\text{ S m}^{-1}$ , high affinity between the silver and chalcogenides and correlation among silver ions are suggested by the large chemical shift and by the scalar coupling, respectively.

## Introduction

The spin–lattice relaxation time,  $T_1$ , of silver nuclei in silver ion conductors is much shorter than other silver compounds because of a large fluctuation of field caused by the ion transport. But which mechanism causes the spin–lattice relaxation mainly is still a matter of debate.<sup>1–3</sup> For example, it is reported that in the case of  $\beta\text{-Ag}_3\text{SBr}$   $T_1$  increases with decreasing Larmor frequency in the fast motional limit,<sup>1</sup> and the relaxation mechanism is interpreted to be the fluctuation of the anisotropic chemical shift. On the contrary, in the case of silver borate glasses doped with silver iodide, the dependence of  $T_1$  on Larmor frequency is very weak.<sup>2</sup>

Recently, we reported the temperature dependences of  $T_1$  of the mobile Ag and immobile Ga of  $\text{Ag}_9\text{GaSe}_6$ , and we found that the experimental  $T_1$  ratio of  $^{107}\text{Ag}$  to  $^{109}\text{Ag}$  is 1.3 and  $T_1$  was not dependent on the magnetic field. As a result, we concluded that the relaxation is dominated by the scalar coupling between the silver nuclei, and the  $T_1$  ratio of 1.3 results from the scalar coupling by the equation

$$T_{1\alpha}^{-1}/T_{1\beta}^{-1} = \gamma_\alpha^2/\gamma_\beta^2 \quad (1)$$

$\gamma_\alpha$  and  $\gamma_\beta$  are the gyromagnetic ratios of each spin, where  $\alpha$  and  $\beta$  correspond to the nuclei of  $^{109}\text{Ag}$  and  $^{107}\text{Ag}$ , respectively.<sup>3</sup> We have also found the following relations among the activation energies,

$$E(T_1(\text{Ag}), 18\text{ MHz}) < E(\sigma, 1.6\text{ Hz}) = E(T_1(\text{Ga}), 100\text{ MHz}) \quad (2)$$

where  $E(T_1(\text{Ag}), 18\text{ MHz})$  is an activation energy given by  $T_1$  of  $^{109}\text{Ag}$  at 18 MHz,  $E(\sigma, 1.6\text{ Hz})$  is an activation energy given by the measurement of the ionic conductivity,  $\sigma$ , and  $E(T_1(\text{Ga}), 100\text{ MHz})$  is an activation energy given by  $T_1$  of  $^{71}\text{Ga}$  at 100 MHz.

It is known that most of the argyrodite group compounds represented by  $\text{Ag}_{7-9}\text{MX}_6$  ( $M = \text{metal}$  and  $X = \text{chalcogenide}$ ) such as  $\text{Ag}_9\text{GaSe}_6$  have the same space group ( $F43m$ , cubic, named phase I)<sup>4–8</sup> at room temperature and show a high ionic conductivity of  $0.1\text{--}1\text{ S m}^{-1}$ .<sup>4–8</sup> In this structure, the silver ions are distributed statistically at three sites.<sup>6</sup> As regards  $\text{Ag}_7\text{NbS}_6$ , three phases are observed at room temperature, around 245 K, and around 100 K, and this room-temperature phase belongs to the same crystal group.<sup>4</sup> Therefore, to confirm that the scalar coupling dominates the magnetic relaxation in the  $\text{Ag}_{7-9}\text{MX}_6$  type compounds, the temperature dependences of  $T_1$  of  $^{109}\text{Ag}$ ,  $^{107}\text{Ag}$ , and  $^{93}\text{Nb}$  have been measured for  $\text{Ag}_7\text{NbS}_6$  and  $T_1$  of  $^{109}\text{Ag}$  NMR has been measured for  $\text{Ag}_7\text{TaS}_6$ .<sup>5</sup> Also,  $^{109}\text{Ag}$  chemical shifts of  $\text{Ag}_7\text{NbS}_6$ ,  $\text{Ag}_7\text{TaS}_6$ ,  $\text{Ag}_9\text{GaSe}_6$ ,<sup>6</sup>  $\text{Ag}_8\text{-SiTe}_6$ ,<sup>7</sup> and  $\text{Ag}_8\text{GeTe}_6$ <sup>7</sup> have been measured and compared to other silver ion compounds.

## Experimental Section

A polycrystalline sample of  $\text{Ag}_7\text{NbS}_6$  was prepared by heating a mixture of  $\text{Ag}_2\text{S}$ ,  $\text{NbS}_2$ , and S in an evacuated silica tube at  $500\text{--}550\text{ }^\circ\text{C}$  for 4 days.<sup>4</sup> Also,  $\text{Ag}_7\text{TaS}_6$ ,  $\text{Ag}_9\text{GaSe}_6$ ,  $\text{Ag}_8\text{SiTe}_6$ , and  $\text{Ag}_8\text{GeTe}_6$  were prepared in a similar way. Throughout all experiments, exactly the same sample for each compound was used.

A Bruker MSL-400 NMR spectrometer (9.39 T) was used for most of the measurements. An aqueous solution of  $\text{AgNO}_3$  with  $\text{Fe}(\text{NO}_3)_3$ <sup>9,10</sup> was used as the reference material of the chemical shift of  $^{109}\text{Ag}$ .  $T_1$  of  $^{109}\text{Ag}$  and  $^{107}\text{Ag}$  were measured by the saturation recovery method, and  $T_1$  of  $^{93}\text{Nb}$  was measured by the inversion recovery ( $180^\circ\text{-}\tau\text{-}90^\circ$ ) method. To measure the magnetic field dependence of  $T_1$  of  $^{109}\text{Ag}$ , a Bruker MSL-300 spectrometer was used.

## Results

At room temperature, motional narrowing of the  $^{109}\text{Ag}$  line shape in all the measured samples has been completed, and the chemical shifts can be obtained precisely. Table 1 compares

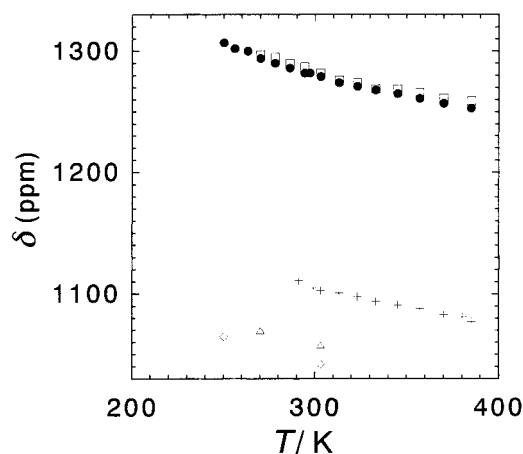
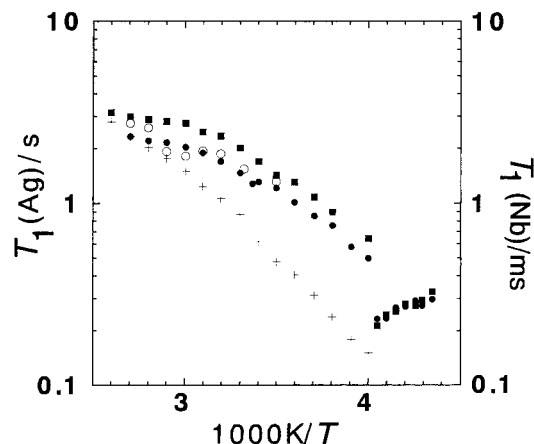
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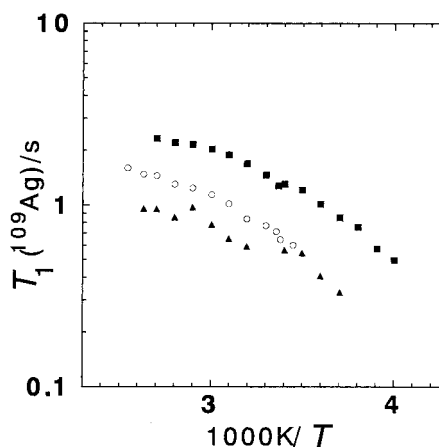
**TABLE 1:**  $^{109}\text{Ag}$  NMR Chemical Shifts,  $\delta$  (ppm)

compound	$\delta$ (ppm)	compound	$\delta$ (ppm)
$\text{Ag}_7\text{NbS}_6$	1282 <sup>a</sup>	$\text{KAg}_4\text{I}_5$	810 <sup>b</sup>
$\text{Ag}_7\text{TaS}_6$	1287 <sup>a</sup>	$\text{RbAg}_4\text{I}_5$	790 <sup>b</sup>
$\text{Ag}_9\text{GaSe}_6$	1105 <sup>a</sup>	$\text{Ag}_{26}\text{I}_{18}\text{W}_4\text{O}_{16}$	580 <sup>b</sup>
$\text{Ag}_8\text{SiTe}_6$	1056 <sup>a</sup>	AgI-doped glasses	400–630 <sup>c,d</sup>
$\text{Ag}_8\text{GeTe}_6$	1040 <sup>a</sup>	AgI-alkylammonium	800 <sup>d</sup>
AgF (solid)	−110 <sup>b,e</sup>	AgF (solution)	430 <sup>b,f</sup>
AgCl (solid)	370 <sup>b,e</sup>	AgCl (solution)	495 <sup>b,f</sup>
AgBr (solid)	350 <sup>b,e</sup>	AgBr (solution)	585 <sup>b,f</sup>
AgI (solid)	710 <sup>b,e</sup>	AgI (solution)	790 <sup>b,f</sup>

<sup>a</sup> This work. <sup>b</sup> Reference 10. <sup>c</sup> Reference 11. <sup>d</sup> Reference 12. <sup>e</sup> Reference 13. <sup>f</sup> Reference 14.

**Figure 1.** Temperature dependences of the  $^{109}\text{Ag}$  chemical shift,  $\delta$ , for  $\text{Ag}_7\text{TaS}_6$  ( $\square$ ),  $\text{Ag}_7\text{NbS}_6$  ( $\bullet$ ),  $\text{Ag}_8\text{GaSe}_6$  ( $+$ ),  $\text{Ag}_8\text{SiTe}_6$  ( $\triangle$ ), and  $\text{Ag}_8\text{GeTe}_6$  ( $\diamond$ ).**Figure 2.** Temperature dependences of  $T_1$  for  $^{107}\text{Ag}$  ( $\blacksquare$ ),  $^{109}\text{Ag}$  ( $\bullet$ ), and  $^{93}\text{Nb}$  ( $+$ ) NMR at 9.39 T and  $T_1$  for  $^{109}\text{Ag}$  ( $\circ$ ) at 7.05 T in  $\text{Ag}_7\text{NbS}_6$ .

the chemical shifts of the  $\text{Ag}_{7-9}\text{MX}_6$  type compounds with those of other silver compounds.<sup>10–14</sup> The shifts are much larger than those of other silver compounds, including silver ionic conductors. Figure 1 shows the temperature dependence of the chemical shift of  $^{109}\text{Ag}$  of  $\text{Ag}_7\text{NbS}_6$ , and the temperature coefficient is  $-0.5$  to  $-0.3$  ppm/K. Figure 2 shows the temperature dependences of  $T_1$  of  $^{109}\text{Ag}$ ,  $^{107}\text{Ag}$ , and  $^{93}\text{Nb}$  of  $\text{Ag}_7\text{NbS}_6$ . Because of the fast ionic motion in the phase I, we cannot observe the  $T_1$  minimum even with as low a frequency as 18 MHz.<sup>3</sup>  $T_1$  of  $^{109}\text{Ag}$  is independent of the external magnetic field, and the ratio of  $T_1(^{109}\text{Ag})^{-1}/T_1(^{107}\text{Ag})^{-1}$  is 1.3.<sup>3</sup> The temperature dependences of  $T_1$  of the mobile  $^{109}\text{Ag}$  and  $^{107}\text{Ag}$  spins are weaker than that of the immobile  $^{93}\text{Nb}$ . Activation energies can be obtained roughly from the straight parts just

**Figure 3.** Temperature dependences of  $T_1$  of  $^{109}\text{Ag}$  for  $\text{Ag}_7\text{NbS}_6$  ( $\blacksquare$ ),  $\text{Ag}_7\text{TaS}_6$  ( $\blacktriangle$ ), and  $\text{Ag}_9\text{GaSe}_6$  ( $\circ$ ).

above the phase transition temperature in  $\log(T_1/\text{s})$  vs  $T^{-1}$  plots. The values are  $0.14 \pm 0.01$  eV ( $T_1(\text{Ag})$ ) and  $0.21 \pm 0.01$  eV ( $T_1(\text{Nb})$ ), and they are smaller than the activation energy of  $0.25 \pm 0.03$  eV obtained from the conductivity measurement.<sup>4</sup>  $T_1$  of the Ag of  $\text{Ag}_7\text{NbS}_6$ ,  $\text{Ag}_7\text{TaS}_6$ , and  $\text{Ag}_9\text{GaSe}_6$  are of the same order of magnitude (Figure 3).

The line width of Ag in phase II is about 200 ppm, because the motional narrowing is not completed, and  $T_1$  of the Ag nuclei decreases with increasing temperature since silver ionic motion is slower than 18 MHz and much slower than that in the phase I (Figure 2).

## Discussion

**Chemical Shifts.** It is well-known that the chemical shift of a metal ion depends on the type of the adjacent ligands and the coordination number.<sup>15</sup> The most important term which is dependent on the ligands causes paramagnetic shielding. In the case of Ag, the shielding increases with the increase of the electron-donating ability of the ligand to the 5p orbital of silver and with the increase of the electron acceptability of the ligand from the 4d orbital of silver.<sup>16</sup> In the case of a silver complex solution, it is pointed out experimentally that the magnetic shielding corresponds well to the order of stability represented by formation energy of the silver ligand.<sup>15</sup> In the  $\text{Ag}_{7-9}\text{MX}_6$  type compound, the immobile metals are surrounded by four chalcogenides ions, and for the discussion of the chemical shift of silver, the effect of the immobile metal ions can be neglected. The logarithm of the formation constant of  $\text{Ag}(\text{SH})_2^-$  is 17.7<sup>17</sup> and is larger than the value of 14.93 of  $\text{AgI}_4^{3-}$ .<sup>15,17</sup> The large chemical shift of  $\text{Ag}_7\text{NbS}_6$  corresponds to the above phenomenological relation.<sup>15</sup> In the  $\text{Ag}_{7-9}\text{MX}_6$  type compounds, the number of silver ions in the bipyramidal center is nearly the same as that in the center of the tetrahedron constructed by the chalcogenides,<sup>4–8</sup> and the ratio of the number changes with the temperature.<sup>8</sup> Therefore, it is likely that the change in the population makes a contribution to the dependence of the chemical shift.

**Relaxation Time.** The dipolar interaction can be neglected on the basis of order of magnitude calculations of the possible contributions to  $T_1$ . Presumably, the relaxation due to paramagnetic impurity has to be considered, but because of the temperature dependence of  $T_1$  of Ag, it is unlikely that the coupling with a paramagnetic ion is the main relaxation. If the fluctuation of anisotropic chemical shift is the dominant term of the magnetic relaxation mechanism of Ag nuclei,  $T_1$  measured at 7.05 T must be  $(4/3)^2 = 1.78$  times  $T_1$  measured at 9.39 T.<sup>1</sup>

However,  $T_1$  of  $^{109}\text{Ag}$  of Ag<sub>7</sub>NbS<sub>6</sub> (Figure 1) is not dependent on the external field as  $T_1$  in Ag<sub>9</sub>GaSe<sub>6</sub> was.<sup>3</sup> This indicates that the anisotropic chemical shift is not the dominant mechanism in this case. Here, we consider the case that the scalar coupling contributes mainly to the relaxation. Among the three types of couplings [Ag–Ag, Ag–Nb, and Ag–S] for Ag<sub>7</sub>NbS<sub>6</sub>, the coupling of Ag–S has to be denied because  $^{32}\text{S}$  has no nuclear spin and has a natural abundance of almost 100%. Since the room-temperature phases of the silver ionic conductors, Ag<sub>7</sub>NbS<sub>6</sub>, Ag<sub>7</sub>TaS<sub>6</sub>, and Ag<sub>9</sub>GaSe<sub>6</sub>, all show  $T_1$  of the same order magnitude for Ag (Figure 3), the coupling of Ag–Se is not probable as the main source of the relaxation. In the case of scalar coupling of the second kind for Ag–Nb or Ag–Ga, the correlation times must be equal to  $T_1$  of the quadrupole nuclei such as Nb or Ga. Because  $T_1$  of Nb or Ga is on the order of  $10^{-4}$ – $10^{-3}$ s, the correlation times of scalar coupling become  $10^{-4}$ – $10^{-3}$ s. Since  $T_1$  of Ag is in the fast motional limit and this correlation time must be much shorter than  $10^{-4}$ – $10^{-3}$ s, it is unlikely that scalar coupling of the second kind makes a contribution to the observed  $T_1$ . Therefore, only the possibility of scalar coupling of Ag–Ag remains. Though the experimental ratio of  $T_1(^{107}\text{Ag})^{-1}/T_1(^{109}\text{Ag})^{-1} = 1.3$  is explained for  $\beta$ -Ag<sub>3</sub>SBr by an anisotropic chemical shift,<sup>1</sup> it can be also explained by scalar relaxation of first kind between Ag–Ag using eq 1.<sup>3</sup> Hence, we can say that the scalar coupling is the dominant term of the magnetic relaxation in the Ag<sub>7-9</sub>MX<sub>6</sub> type compounds.

**Activation Energy.** The activation energy obtained from the mobile  $^{109}\text{Ag}$  measured at 18 MHz is  $0.14 \pm 0.01$  eV, and that obtained from immobile  $^{93}\text{Nb}$  measured at 100 MHz is  $0.21 \pm 0.01$  eV. The conductivity measurement gave a larger value of  $0.25 \pm 0.03$  eV.<sup>4</sup> So, the following inequality is obtained,

$$E(T_1(\text{Ag}), 18 \text{ MHz}) < E(T_1(\text{Nb}), 100 \text{ MHz}) < E(\sigma, 1.6 \text{ Hz}) \quad (3)$$

We must note that the activation energy obtained from immobile Ga nucleus was nearly equal to that from conductivity measurement.<sup>3</sup> It is well-known that the activation energy measured at a higher frequency is generally larger than that measured at a lower frequency.<sup>18</sup> So,  $E(T_1(\text{Nb}), 100 \text{ MHz}) < E(\sigma, 1.6 \text{ Hz})$  is acceptable. It is seemed that the inequalities of  $E(T_1(\text{Ag}), 18 \text{ MHz}) < E(T_1(\text{Nb}), 100 \text{ MHz})$  and  $E(T_1(\text{Ag}), 18 \text{ MHz}) <$

$E(T_1(\text{Ga}), 100 \text{ MHz})$  are valid, because the  $T_1$  of Ag is dominated by the fluctuation of scalar coupling between silver and silver, and  $E(T_1(\text{Nb}), 100 \text{ MHz})$  corresponds to the translational self-diffusion of silver ions. Since chemical bonds are needed for scalar coupling, probably  $E(T_1(\text{Ag}), 18 \text{ MHz})$  must be giving an activation energy for connection or cutting off of either direct chemical bond or indirect chemical bonds such as Ag–S–Ag.

Consequently, although Ag<sub>7</sub>NbS<sub>6</sub> and related compounds show high ionic conductivity of  $0.1$ – $1 \text{ S m}^{-1}$ , high affinity between silver and the chalcogenides and correlation among silver ions are suggested by the large chemical shift and by scalar coupling, respectively.

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