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Electrical Conductivity and Thallium Spin-Lattice Relaxation Time Measurements of Tl_4HgBr_6 and Tl_4HgI_6

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Synopsis. The ionic transport properties of Tl_4HgBr_6 and Tl_4HgI_6 were investigated with ^{205}Tl spin-lattice relaxation time (T_1) and electrical conductivity (σ) measurements. The temperature dependence of ^{205}Tl T_1 shows that Tl^+ ion diffusion is activated at high temperatures in both crystals. The activation energies of diffusion were estimated to be 47 and 55 kJ mol^{-1} for Tl_4HgBr_6 and Tl_4HgI_6, respectively, from the temperature dependence of σ.

The compounds of Tl_4HgBr_6 and Tl_4HgI_6 are isomorphous with each other and crystallize in a tetragonal lattice with the space group of *P4/mnc*.[1—3] In this study we measured the nuclear magnetic relaxation time of ^{205}Tl nuclei and the electrical conductivity as a function of temperature in order to investigate the transport properties of heavy monovalent thallium ions in these crystals.

Experimental

Preparation. The samples were prepared by solid state reactions.[2] A stoichiometric mixture of the binary components was sealed in a silica ampoule in vacuo, melted for ca. 5 h in an electric furnace, and quenched by throwing it into water. Then, the quenched material was annealed at ca. 20 K below the respective peritectic temperatures for 2—3 days. The compounds were characterized by room-temperature X-ray powder diffraction.

Measurements. The electrical conductivity (σ) was measured by complex impedance analysis using an Ando AG-4311 LCR meter over a frequency range of 0.1—100 kHz. The sample used for the σ measurements was pressed into a disc (10 mm diameter and about 2 mm thick). Carbon (Acheson Electrodag 502) was used as electrodes. The NMR spin-lattice relaxation time (T_1) of ^{205}Tl nuclei was measured at 16 MHz by use of a Matec pulse NMR spectrometer with the 180°—*t*—90° pulse sequence.

Results and Discussion

^{205}Tl Spin-lattice Relaxation Time. Because in measurements of ^{205}Tl T_1 the magnetization recovery after the 180° pulse was nonexponential,[4] the T_1 value was determined from the longer part of the magnetization recovery vs. *t* plot. Figure 1 shows the temperature dependence of ^{205}Tl T_1 observed above room temperature for Tl_4HgBr_6. At room temperature T_1 was ca. 1.5 s. With increasing temperature, T_1 gradually decreased up to ca. 400 K, and then rather steeply decreased at temperatures higher than 400 K. This shows that some motion affecting the ^{205}Tl relaxation time begins as the temperature reaches 400 K. At the same time, the free-induction-decay signal showed a narrowing above 400 K, indicating that the motion activated at high temperatures is the translational self-diffusion of the Tl^+ ions.

The temperature dependence of T_1 was analyzed by using

$$T_1^{-1} = AT^n + B\exp(-E_a/RT). \qquad (1)$$

The first term implies T_1 due to lattice vibrations; the *n* parameter is taken as 2.[4] The second term represents the contribution to T_1 of Tl^+ ionic diffusion, and the usual Arrhenius relation is assumed for the motion. By least-squares fitting, the unknown parameters in Eq. 1 were determined to be $A=6.8\times10^{-6}$ s^{-1} K^{-2}, $B=2.1\times10^{6}$ s^{-1}, and $E_a=57$ kJ mol^{-1}. Thus, from NMR measurements the activation energy for Tl^+ ion transport could be determined. The shorter component of the magnetization recovery curve, which was roughly estimated, was shorter by a factor of ca. 30 than the longer component given in Fig. 1 and showed a temperature dependence similar to that of the longer one.

The free-induction-decay signals of ^{205}Tl NMR in Tl_4HgI_6 were very short and, hence, had poor signal-to-noise ratios. Therefore, we gave up to measure the

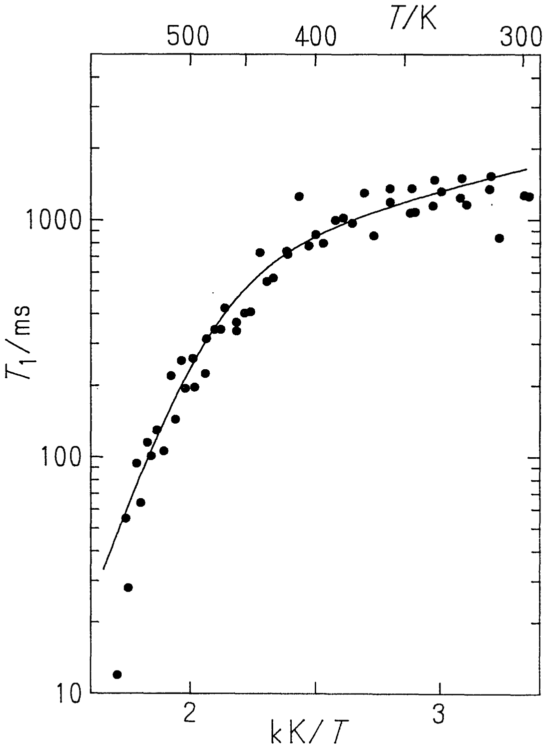

Fig. 1. Temperature dependence of ^{205}Tl spin-lattice relaxation time T_1 measured at 16 MHz for Tl_4HgBr_6. A solid line was calculated by Eq. 1.

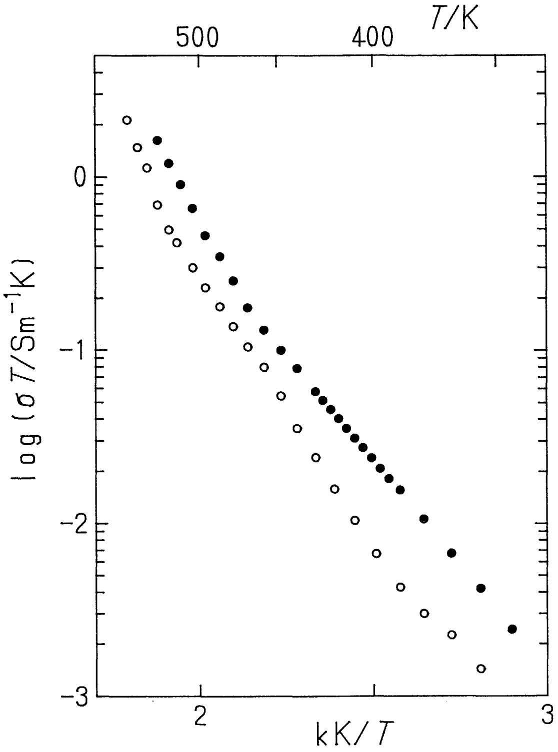

Fig. 2. Temperature dependence of the electrical conductivity σ in Tl_4HgBr_6 and Tl_4HgI_6. Log σT is plotted against $1/T$. ●: Tl_4HgBr_6 and ○: Tl_4HgI_6.

full temperature dependence of T_1, except for several points at high temperatures where the signal was somewhat motionally narrowing. The T_1 value was ca. 40 ms at 510 K and seemed to decrease exponentially upon heating, indicating that the Tl^+ ion diffusion occurs at high temperatures in Tl_4HgI_6 as well.

Electrical Conductivity. The complex impendance plane obtained for both compounds shows a single semicircle slightly depressed downward. Hence, its low-frequency intercept on the Z' axis is defined as the sample resistance. Figure 2 shows the temperature dependence of the electrical conductivity (σ), where log σT is plotted as a function of $1/T$. Upon heating, the σT value of Tl_4HgBr_6 increased exponentially up to ca. 480 K, yielding a conductivity activation energy of 47 kJ mol^{-1}. Near 480 K, a small change in the slope of the log σT vs. $1/T$ curve was recognized. Although this behavior may be assigned to a transition from extrinsic to intrinsic conductivity, the real reason is not apparent.

The σ value of Tl_4HgI_6 was slightly smaller than that of the bromide analog over the whole temperature range studied, and their temperature dependences are similar to each other. The E_a value of the electrical conduction in Tl_4HgI_6 was estimated to be 55 kJ mol^{-1} from the data below 525 K.

Ammlung et al. studied electrical conduction in Tl_4CdI_6 and In_4CdI_6.[5,6] They found that Tl_4CdI_6 is a rather poor electrical conductor. On the other hand, In_4CdI_6 shows electrical conductivities as high as 10^{-3} S m^{-1} at 493 K in the high-temperature phase stable above 481 K. At the phase transition point to the low-temperature phase, the σ value becomes an order of 1.6 less than that of the high-temperature one. Ammlung et al. showed from conductivity measurements with blocking electrodes that though conduction in the high-temperature phase of In_4CdI_6 is mainly ionic or due to the heavy monovalent In^+ ionic-transport, that in the low-temperature phase is almost electronic.[5] The present compounds, Tl_4HgBr_6 and Tl_4HgI_6, yield σ values of 9.2×10^{-4} and 4.6×10^{-4} S m^{-1} at 496 K, respectively, which are comparable to that observed for the high-temperature phase of In_4CdI_6. Although the electronic contribution to the observed σ in Tl_4HgBr_6 and Tl_4HgI_6 was not determined, the ^{205}Tl NMR study indicates that heavy Tl^+ ions undergo translational self-diffusion at high temperatures. It is therfore concluded that the Tl^+ ions are the mobile species which contribute to the high electrical conduction in the Tl_4HgBr_6 and Tl_4HgI_6 crystals.

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