CHEMISTRY LETTERS, pp. 831-834, 1972. Published by the Chemical Society of Japan

SELF-DIFFUSION COEFFICIENTS OF Tl AND Br IN TlBr SINGLE CRYSTAL

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Self-diffusion coefficients of Tl and Br in TlBr single crystal were determined by the radioactive tracers and the serial sectioning technique. The results are as follows,

$D^*_{Tl} = (1.316 \pm 0.013)\ \exp[-(27.44 \pm 0.55)/RT]\ \mathrm{cm^2/sec}$ (420-300°C)

$D^*_{Br} = (1.227 \pm 0.013) \times 10^{-2} \exp[-(17.75 \pm 0.22)/RT]\mathrm{cm^2/sec}$ (420-250°C)

where the activation energy is expressed in unit of kcal/mol.

As a part of the interdiffusion study for the TlBr-TlCl system, the self-diffusion coefficients of Tl and Br in TlBr single crystal were measured by the tracer method in a temperature range of 250 to 420°C.

TlBr, 99.9% pure, was purified further in an evacuated and sealed pyrex-glass tube by the zone-refining technique. The zone-refining was repeated 40 times. The purified TlBr were sealed in a pyrex tube and a single crystal, 0.8-1.0 cm in diameter and about 5 cm long, was grown by Bridgeman method. The disks, 2-3 mm in thickness, were cut from single crystals and polished with emery papers. The thickness and weight of each disk were measured precisely. A few drops of aqueous Tl^*Cl (^{204}Tl) or $NaBr^*$ (^{82}Br) solution were applied to one end of disk and dried by means of a infrared-lamp. The total activity was about 0.1-1.0 μCi. In order to minimize the loss of TlBr by evaporation, the disk was sandwiched between two stainless steel disks, and sealed in an evacuated pyrex-glass ampoule. By this method the weight loss of the sample was supressed less than one-two hundredth of the initial weight. After diffusion-annealing the sample was taken out and the surface layer of side surface was removed by cutting in order to eliminate the effect of vapor phase transfer and surface diffusion of radio isotopes. Then, the disk was sectioned by the successive grinding by means of a grinding machine which was originally designed by Letaw et al.[1)] The thickness of each layer was about 5-50μ. The radioactivity of radio isotopes on the polishing paper was counted by a Geiger-Muller counter for ^{204}Tl and by a scintillation counter for the γ-radiation from ^{82}Br. The logarithm of counts per unit weight was plotted against the square of distance from the surface. The self-diffusion coefficient was determined from the slope and the time of annealing.

The self-diffusion coefficients (D^*) are shown in Fig. 1. The solid lines are the least squares fits to the obtained data. These lines are represented by the following equations,

$$D_{Tl} = (1.316 \pm 0.013) \exp[-(27.44 \pm 0.55)/RT] \ cm^2/sec \ (420\text{-}300°C)$$

$$D_{Br} = (1.227 \pm 0.013) \times 10^{-2} \exp[-(17.75 \pm 0.22)/RT] \ cm^2/sec \ (420\text{-}250°C)$$

where energy is given in unit of kcal/mol and empirical errors are expressed in terms of standard deviation. For comparison, the value of D^*_{Tl} and D^*_{Cl} in TlCl determined by Friauf[2)] and those by the authors are also given in Fig. 1. The agreement between both data is quite satisfactory. It is concluded from this figure that the activatio energy of diffusion of Tl^+ and halogen ions are nearly the same for both ionic crystals. It has been said that the diffusion of ions in TlCl crystal is caused by the vacancy mechanism via Schottky defects. From the similarity of crystal structure and the results of the present work, the same mechanism seems to prevail in the diffusion of ions in TlBr.

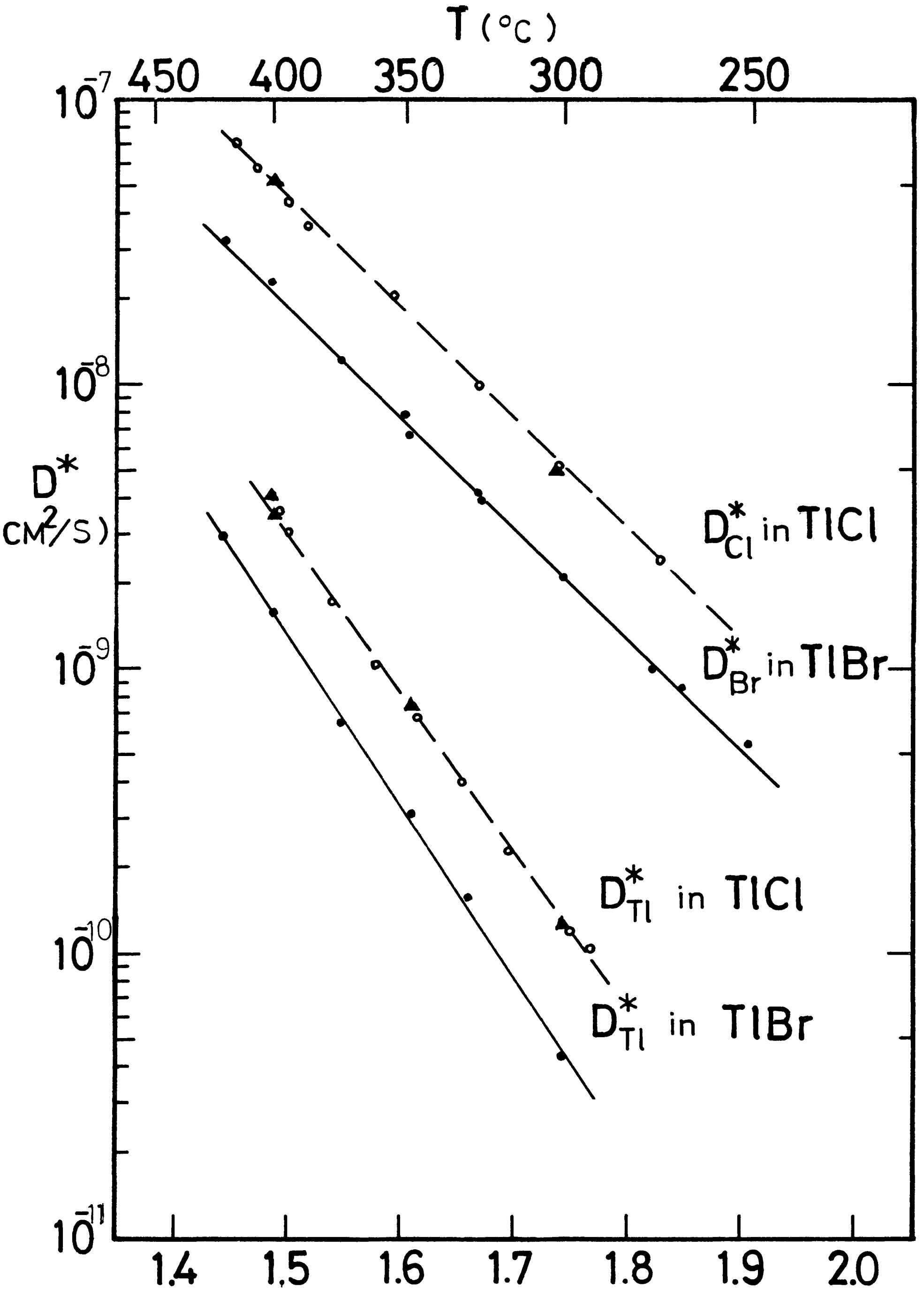

Fig. 1. Self-diffusion coefficient(D*) in TlBr and TlCl

D*(●) in TlBr & D*(▲) in TlCl : this work

D*(○) in TlCl : Friauf 2)

References

1) H. Letaw, J. L. M. Slifkin, and W. M. Portnoy, Rev. Sci. Inst., 25, 865 (1954).

2) R. J. Friauf, Z. Naturforsch., 26a, 7, 1210 (1971).

(Received July 22, 1972)