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Transport Number in Solid Cesium Bromide*

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The transport number of cerium bromide single crystals has been measured over the temperature range 350° to 450°C by the method of Tubandt. No temperature dependence is observed, and the average value of the cation transport number is 0.49±0.05. A preferential growth phenomenon is described, and its possible interference with the measurement is discussed. It is estimated that the true cation transport number may be as low as 0.3 because of this phenomenon.

NOTABLE success has been achieved in recent years in the identification of the processes of transport in ionic crystals.[1] In order to characterize the mechanism of transport in a crystal, knowledge of the transport number is usually vital. The purpose of this note is to describe the results of some measurements of the transport number in cesium bromide. This investigation was carried on in conjunction with self-diffusion and conductivity measurements[2] in an attempt to determine the mechanism of conduction in this material.

The transport number was measured by the method of Tubandt.[3] The experimental arrangement is shown in Fig. 1. The guard electrodes in this case were pressed tablets of barium bromide. It has been determined that this material conducts solely by the motion of anions.[4] The samples of cesium bromide were cut from single crystals supplied by Dr. Karl Korth, Kiel, Germany. A known amount of charge was passed through the tablets. These tablets were weighed before and after electrolysis on an automatic semimicrobalance, and from the changes in weight and the application of Faraday's law, the transport number was determined. In our arrangement, tablets 3 and 4 (considered as a unit) should undergo a weight increase proportional to the transport number; tablets 6 and 7 should experience a corresponding decrease; and tablets 2, 5, and 8 should not change at all.

The transport number of the cation in cesium bromide was measured in this way at several temperatures in the range 350° to 450°C. The results of two typical runs are given in Table I. A total of twelve successful measurements representing 24 separate determinations were made which showed no apparent temperature dependence. The average value of the cation transport number is 0.49±0.05.

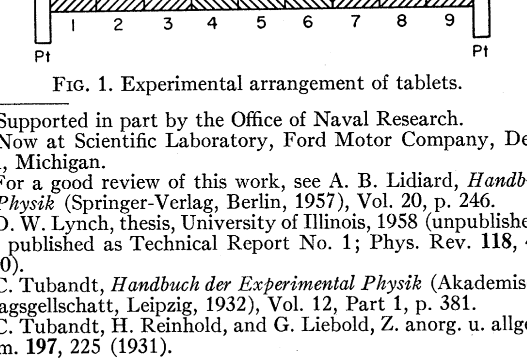

FIG. 1. Experimental arrangement of tablets.

Several complications arose during the course of these experiments which led us to question the validity of the assumptions implicit in Tubandt's equations. It was difficult to make the separation between tablets 4 and 5 or between 5 and 6 after electrolysis. Separation between unlike materials, such as 3 and 4 or 6 and 7, is difficult also, but this was expected and does not interfere with the measurement. The separation between 4, 5, and 6, however, is essential to the measurement as consideration of the equations will show (cf. the following). Small areas which were raised above the rest of the surface were observed on the surfaces of the crystals which face the anode (e.g., the surface of crystal 4 next to 5). Corresponding depressions were visible on the surfaces which face the cathode. Figures 2 and 3, while not revealing directly the vertical extent of the irregularity, do give some idea of the appearance of the surface.

These areas are interpreted as areas of most intimate contact during electrolysis and, hence, of highest current density. It appears that one crystal grows at the expense of the other during electrolysis, and the sense of growth depends upon the direction of the current. A very rough estimate indicates that the amount of material present in the raised areas (or absent from the depressions) is of the same order of magnitude as the measured weight changes of the tablets.

To discuss what effect these depressions might have on the results, we will first derive the transport number

TABLE I. Transport number data for cesium bromide.

	Weight changes (mg)	
	Run 37	Run 44
Tablet 2[a]	+0.19	+0.20
Tablets 3 and 4	+7.78	+7.79
Tablet 5	−0.14	−0.02
Tablets 6 and 7	−7.58	−7.85
Tablet 8	+0.42	+0.09
Temp. (°C)	451	352
Charge (coul)	7.34	7.48
t_+ (computed from 3 and 4)	0.480	0.476
t_+ (computed from 6 and 7)	0.468	0.472

[a] For identification of tablets, see Fig. 1.

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[1] For a good review of this work, see A. B. Lidiard, *Handbuch der Physik* (Springer-Verlag, Berlin, 1957), Vol. 20, p. 246.

[2] D. W. Lynch, thesis, University of Illinois, 1958 (unpublished). Also published as Technical Report No. 1; Phys. Rev. **118**, 468 (1960).

[3] C. Tubandt, *Handbuch der Experimental Physik* (Akademische Verlagsgellschatt, Leipzig, 1932), Vol. 12, Part 1, p. 381.

[4] C. Tubandt, H. Reinhold, and G. Liebold, Z. anorg. u. allgem. Chem. **197**, 225 (1931).

FIG. 2. Example of isolated depression, approximately 160×.

equations as normally considered, and then alter them to account for the preferential growth phenomenon. Consider tablets 3 and 4. These are normally weighed together, and are to be considered as a unit. A Faraday equivalent of bromine enters 3 from 2 for each coulomb of charge passed. The charge will be transported at the other interface between tablets 4 and 5 by both ions, so that we expect somewhat less than a Faraday equivalent of cesium to enter 4 from 5 and a supplementary amount of bromine to leave 4 for 5. The fractions defined in this scheme are the transport numbers of the two ions. We can write for the change of weight of tablets 3 and 4

$$\Delta W=(M_{\mathrm{Br}}-M_{\mathrm{Br}}t_{-}+M_{\mathrm{Cs}}t_{+})Q/96\,500,$$

where the M's are the atomic weights, the charge Q is in coulombs, and the weight change ΔW is in grams. Since the sum of the transport numbers is unity, we can rewrite this as:

$$\Delta W=(M_{\mathrm{Br}}+M_{\mathrm{Cs}})t_{+}Q/96\,500.$$

We have tacitly assumed that both ions are able to wander freely across the boundary between the crystals. It is also important to note that the identity of the interface must be preserved for these relations to be valid, a condition which may not be satisfied in our experiments.

As a possible explanation for the effects observed, we suggest that, although both ions move within the crystal, one ion (in this case, bromine) has much more difficulty crossing the interface than the other. In the limiting case in which the bromine ion cannot cross the interface at all, we shall obtain a new expression for the transport number. The analysis is the same as before except for the term corresponding to the motion of bromine from 4 to 5. In this case, we have

$$\Delta W=(M_{\mathrm{Br}}+M_{\mathrm{Cs}}t_{+})Q/96\,500.$$

If we use this expression to analyze our data, we arrive at a figure of about 0.3 for t_{+}.

FIG. 3. Example of isolated raised area, approximately 160×.

It is interesting to note that if one uses Lynch's[5] data on the diffusion coefficients to calculate a transport number, assuming only that both ions move by the same mechanism, one arrives at a value of t_{+} near 0.3. This assumption is not valid as Lynch points out, but using any reasonable set of mechanisms which might explain his data will not lead to a transport number much different from 0.3.

It would seem likely that the situation which actually obtains is intermediate to these two extremes, that is to say, some bromine crosses the interface, and some remains behind to nucleate new crystal. The details are probably dependent on the condition of the surface, although several attempts at altering the surface (different orientations, degrees of polish, etc.) did not change the experimental results.

It is interesting to note that Kerkhoff[6] found that in very pure KCl, under conditions in which the transport number was very different from unity, the crystals stuck together badly. It is possible that he was dealing with an effect similar to the one described here, which might explain his remarkably low values of the cation transport number. These results have been discussed in a review article by Seitz.[7] It is possible that such effects occur whenever both ions participate in conduction to a comparable extent. For we can characterize our explanation of the effect by saying that the ratio of the jump probabilities of the two ions across the interface is different from what it is in the interior of the crystal. The transport number will be unambiguous whenever these ratios are equal, a situation which occurs when one ion is solely responsible for the charge transport.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge many fruitful discussions of this work with Professor R. J. Maurer and with Dr. David W. Lynch. The support of a Corning Glass Works Foundation Fellowship is gratefully acknowledged.

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[5] Reference 2, p. 56.

[6] F. Kerkhoff, Z. Physik **130**, 449 (1951).

[7] F. Seitz, Revs. Modern Phys. **26**, 20 (1954).

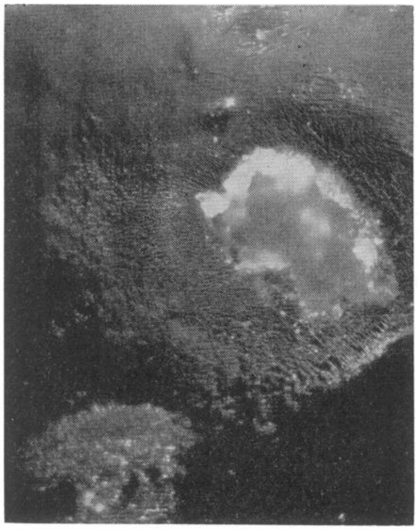

FIG. 2. Example of isolated depression, approximately 160×.

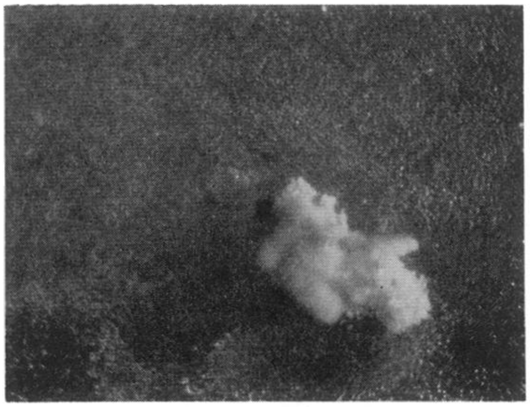

FIG. 3. Example of isolated raised area, approximately 160×.