BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 359—361 (1972)

Self-Diffusion of Chloride Ions in Manganese Dichloride Crystallites

Yoshihiro Sensui

Institute for Atomic Energy, Rikkyo (St. Paul's) University, Yokosuka

(Received June 19, 1971)

The self-diffusion of chloride ions in the powdery crystals of manganese dichloride was studied in the temperature range of 200—420°C by the use of the isotopic-exchange method. The activation energies for self-diffusion were determined to be 0.95 and 1.6 eV in a lower and a higher temperature region respectively. From these, the activation energy for the migration of chloride ions and the formation energy of an anion vacancy or a pair of an anion and a cation vacancy were deduced.

The method of the isotopic-exchange reaction between gaseous molecules and ionic crystals is very useful to the investigation of the self-diffusion of ions in crystals. By this method, the self-diffusion of halide ions in alkali halide crystals has been investigated by several workers[1–5] Laurent and Benard[1] and Barr *et al.*[2–4] have studied mainly the diffusion in the bulk of the crystals, while Takaishi and the present author have studied that of chloride ions in the bulk of sodium chloride and rubidium chloride crystallites, along with the surface exchange reaction[5]. There have, however, been few studies of higher valent metal halide crystals, except for the qualitative studies by Willard and his co-workers.[6–8]

In the present work, the self-diffusion of chloride ions in manganese dichloride crystallites was investigated as a first step in the study of a series of higher valent metal chlorides; we chose this material because it is relatively easy to handle because of its layer structure, its low volatility, and presumed surface homogeneity. Larher studied the adsorption of krypton on several kinds of crystallites with $CdCl_2$-type structures and concluded that their surface were very homotattic.[9] Manganese dichloride, which he did not study has the same structure and may be presumed to have a homotattic surface on the basis of the electron microscopic data (Fig. 1).

Experimental

The apparatus and technique for measuring the self-diffusion of chloride ions by the isotopic-exchange method were described in previous papers.[5] The diffusion measurements were carried out on five specimens of powdery crystals.

Radioactive manganese dichloride was prepared in the form of an aqueous solution from radioactive hydrochloric acid distilled in a vacuum and manganese dichloride (Merks G.R.-reagent, Item No. 5927) by the isotopic-dilution method. In the resultant radioactive chloride, the ratio of ^{36}Cl to Cl was 5.3×10^{-4}.

Anhydrous crystallites of radioactive manganese dichloride were prepared by modifying Marshall's method,[10] *i.e.*, by pouring 100 m*l* of distilled ethyl ether into about 2 m*l* of an anhydrous ethanol solution of manganese dichloride and then baking the precipitate at 420°C for 6 hr in vacuum (3×10^{-7} Torr) prior to the experiment. An electronmicrograph of the anhydrous specimen is shown in Fig. 1. The characteristic layer structure appeared even in the external shape of the crystallites.

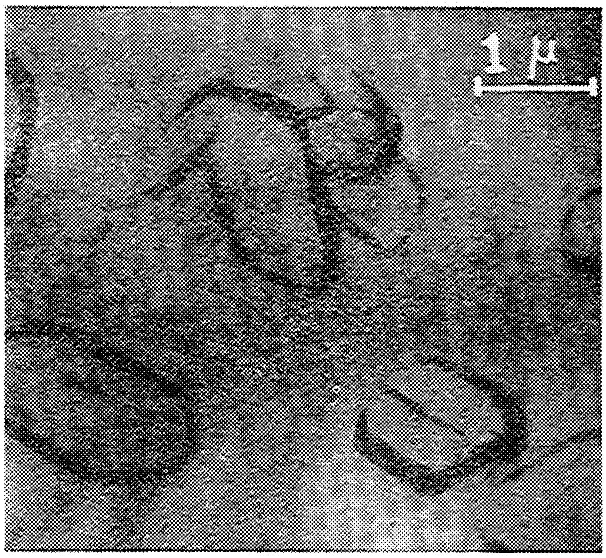

Fig. 1. The external shape of the manganese dichloride crystallites used in the present experiment.

Results and Discussion

Manganese dichloride melts at 650°C and begins to sublime at about 450°C in a vacuum. Therefore, the anion-diffusion measurements were carried out in the temperature range between 200 and 420°C.

At the initial stage of the reaction, only chloride ions near the surface region participate. Accurate data with manganese dichloride were not obtained in this stage, in contrast with the case of alkali chlorides, but it was concluded that the reaction proceed at a high rate. At the later stage, the reaction may be rate-controlled by the bulk-diffusion process. The mean length of the shorter edge of the layer-structural crystallites is estimated from the electronmicroscopic

---

[1] J. F. Laurent and J. Benard, *J. Phys. Chem. Solids*, Pergamon Press **3**, 7 (1957).

[2] L. W. Barr, I. M. Hoodless, J. A. Morrison, and R. Rudham, *Trans. Faraday Soc.*, **56**, 697 (1960).

[3] L. W. Barr, J. A. Morrison, and P. A. Schroeder, *J. Appl. Phys.*, **36**, 624 (1965).

[4] L. W. Barr and D. K. Dawson, *Phys. and Chem. of Ceramic Surfaces, Proceeding* 5 (British Ceramic Soc.), 77 (1965).

[5] T. Takaishi and Y. Sensui, *Trans. Faraday Soc.*, **65**, 131 (1969); *Surface Science*, **19**, 339 (1970).

[6] M. Blau, W. T. Carnall, and J. E. Willard, *J. Amer. Chem. Soc.*, **74**, 5762 (1952).

[7] R. A. Howald and J. E. Willard, *ibid.*, **77**, 2046 (1955).

[8] J. R. Wilson and J. E. Willard, *J. Phys. Chem.*, **70**, 1665 (1966).

[9] Y. Larher, *ibid.*, **72**, 1847 (1968).

[10] F. G. Marshall, *Phys. Rev.*, **58** 642 (1940).

data to be about 0.5 μ (*cf.* Fig. 1). This length corresponds to a few thousand layer in the direction of the *c*-axis of the crystal. In the present experiments, only the ^{36}Cl ions in the bulk of the near-surface gaseous phase; *i.e.*, amounts corresponding to less than 50 layers were counted. Therefore, the diffusion data obtained may be analyzed on the basis of the model of semi-infinite media. For this model, the diffusion equation has the solution;[11]

$$X_g = X_s + 2\alpha(Dt/\pi)^{1/2}$$

where X_g designates the number of ^{36}Cl ions diffused out into the gaseous phases after time t; X_s, that of the ^{36}Cl ions in the surface region which diffused out into the gaseous phase at the initial stage of the reaction; D, the bulk diffusion constant; and α, the product of the surface area and the initial concentration of ^{36}Cl. Denoting the measured counting rate by C, we obtain;

$$C = K\cdot X_g$$

and; $$C_s = K\cdot X_s$$

where K is the conversion factor. Thus, we obtain;

$$C = C_s + \frac{2\alpha}{K}\cdot\left(\frac{Dt}{\pi}\right)^{1/2}$$

in which the value for C_s cannot be obtained directly from experiments. The exchange process may be expected to be rate-controlled by the bulk-diffusion, and the curve of C against $\sqrt{t}$ may be linear, except at the initial stage. However, there are some ambiguties as to the start of the reaction. The measured time, t, must be corrected; that is, t is replaced by $(t+\delta)$, where the value of δ is determined empirically so as to give a linear curve. The results are given in Fig. 2, in which the intersection of the straight line with the coordinate give the value of C_s.

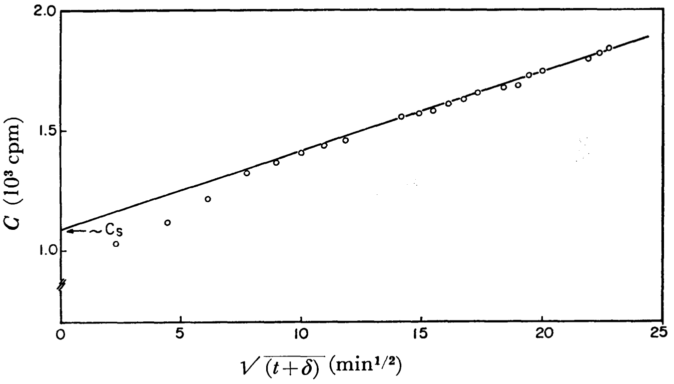

Fig. 2. The plots of C against the square-root of $(t+\delta)$. The data are obtained from the specimen IV at 200°C.

Next, let us suppose that a first diffusion run is made for time t_1 at a temperature T_1 at which the diffusion constant is D_1. If a second run is made for t_2 at a different temperature T_2 (the constant is new D_2), the total counting rate, C, may be shown to be;[11]

$$C = C_s + \frac{2\alpha}{\sqrt{\pi}\cdot K}\cdot(D_1t_1+D_2t_2)^{1/2}.$$

This may be extended to further runs and rewritten as follows;

$$(C-C_s)^2 = \frac{4\alpha^2}{\pi K^2}\cdot(D_1t_1+D_2t_2+\cdots).$$

The values of $(C-C_s)^2$ thus obtained are plotted against the time in Fig. 3. The measured points lie well on the straight lines. If the crystallites contained a lot of dislocations along which diffusion proceeded much faster, complex curve be obtained; that is, the plots of $(C-C_s)^2$ against the time should not fall a straight line when the temperature is changed. This is not the present case, and so it may be concluded that the present model is adequately supported experimentally.

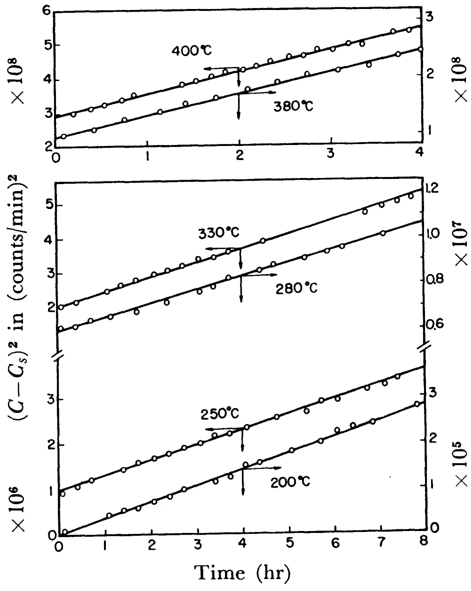

Fig. 3. The plots of $(C-C_s)^2$ against time. All data in this figure are obtained from the specimen IV.

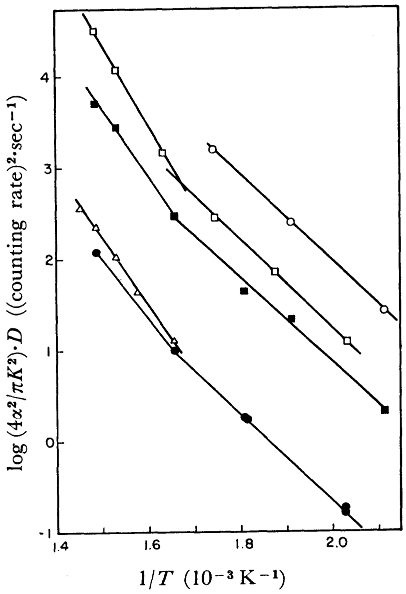

Fig. 4. The Arrhenius plots of apparent self-diffusion rates. ○, ●, □, ■, and △ refer to different specimens, I, II, III, IV, and V respectively.

---

[11] A. B. Lidiard and K. Tharmalingam, *Discuss. Faraday Soc.*, **28**, 64 (1959).

From the slopes of $(C-C_s)^2$ against the time, the values of $(4\alpha^2/\pi K^2)\cdot D$ can be obtained. The Arrhenius plots of these values are shown in Fig. 4, in which all the curves have break at about 330°C and two kinds of slopes are found. The temperature of the break-point is considerably lower than in the case of alkali chlorides.[1-3] The slope in the lower-temperature region in Fig. 4 gives the activation energy, ΔE, for the migration of ^{36}Cl ions, while that in the higher-temperature region gives $(\Delta E+\Delta W)$, where ΔW denotes the formation energy of an anion vacancy, or a half of that of an anion and a cation vacancy. The values for the activation energies of all the specimens are given in Table 1. The absolute value of D depends on the surface area of the specimen, which was not controlled in the present experiment. Hence, it was possible to determine with confidence only the activation energy in the diffusion process, not the frequency factor. However, if crude estimation from the electronmicroscopic data are used for the surface area of the sample, values, 2×10^{-3} cm² sec⁻¹ and 1×10^{-8} cm² sec⁻¹, are given to the frequency factors corresponding to the formation of a vacancy and the migration of ^{36}Cl respectively. Both of these values are small in comparison with the corresponding values[5] in the crystallites of alkali chlorides, but they are not unreasonable.

TABLE 1. THE VALUE OF ACTIVATION ENERGY FOR EACH SPECIMEN

Specimen	ΔE (eV)	$\Delta E+\Delta W$ (eV)
I	0.95	
II	0.95	
III	0.96	1.77
IV	0.95	1.50
V		1.58
Average	0.95	1.6

The author's sincere thanks are due to Professor Dr. T. Takaishi of Rikkyo (St. Paul's) University for his valuable discussions.