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The Self-diffusion of Chloride Ions in Divalent Metal Chloride Crystallites with $CdCl_2$-type Structure

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The self-diffusion of chloride ions in $MgCl_2$- and $CoCl_2$-crystallites with the $CdCl_2$-type structure was studied, the results being compared with previous data on $MnCl_2$ and $NiCl_2$. The diffusion rate was measured through gas/solid-isotopic exchange reactions in a carefully cleaned vacuum system. The results were analyzed by the use of a model of semi-infinite crystal. The Arrhenius plots of apparent diffusion coefficient consist of two segments of line, from whose slopes the activation heat of migration E and the apparent heat of formation of vacancies H_v/n_v are determined. [H_v denotes the total heat of formation of two anion vacancies and one catoin vacancy with $n_v=$ 2 or 3.] The values for E and H_v/n_v were 0.55 and 1.1 eV in $MgCl_2$ and 1.3 and 2.0 eV in $CoCl_2$, respectively. A linear relationship holds between the logarithms of pre-exponential factor of the diffusion coefficient and E or $(E+H_v/n_v)$; *viz.*, the theta-rule holds in this case. In the initial stage of the exchange reaction, ions or atoms in the surface region of crystals were observed to easily migrate. Sodium ions doped deliberately as impurity enhance the diffusion of chloride ions. It is concluded that the diffusion takes place through the vacancy mechanism.

Chemical processes in solids are closely related to migration of atoms or ions in crystals, which is controlled by imperfections in the crystal. The isotopic exchange reaction between crystals and gaseous molecules is one of the simplest surface reactions, and can be used as a useful means of measuring the self-diffusion of ions in crystals. Although diffusion is studied through measurements of electric conductance, it is desirable to confirm the validity of diffusion law by the tracer method.

Most studies on the self-diffusion of anions in solids have dealt with alkali halides, and a few with polyvalent metal halides.[1-3] Dearth of data on the latter crystals may be ascribed to the following. Most of such crystals are easily hydrated and volatile when dehydrated, making the manipulation of samples difficult. Chemical bonds in these crystals are partly ionic and partly covalent,[4] and theoretical interpretations of experimental data may not be as straightforward as in pure ionic crystals. As for theoretical studies, only rough ideas were applied to polyvalent metal fluoride.[5]

In the present paper, the results of studies of the self-diffusion of Cl^- ions in $MgCl_2$- and $CoCl_2$-crystallites with the $CdCl_2$-type structure are compared with the results on $MnCl_2$[2] and $NiCl_2$.[3] Some of these crystals are used as solid catalysts for chlorination of hydrocarbons in gaseous phase.[6]

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[1] G. M. Hood and J. A. Morrison, *J. Appl. Phys.*, **38**, 4796 (1967).

[2] Y. Sensui, This Bulletin, **45**, 359 (1972).

[3] Y. Sensui, *ibid.*, **45**, 2677 (1972).

[4] L. Pauling, "Nature of the Chemical Bond," Third Edition, Cornell University Press, New York (1960).

[5] A. D. Franklin, *J. Phys. Chem. Solids*, **26**, 933 (1965).

[6] T. Shiba, (ed.), "Catalytic Engineering Vol. IX," Chijinshokan & Co., Ltd., Tokyo (1965).

Experimental

Apparatus and General Procedure. The apparatus used was made of Hario-glass, except for the two Teflon stoppers in the circulation pump (Fig. 1). The system consists of a reaction vessel, a thin-wall-type G.M. counter, a circulation pump, a Bourdon-type pressure gauge and a supplier of chlorine gas.

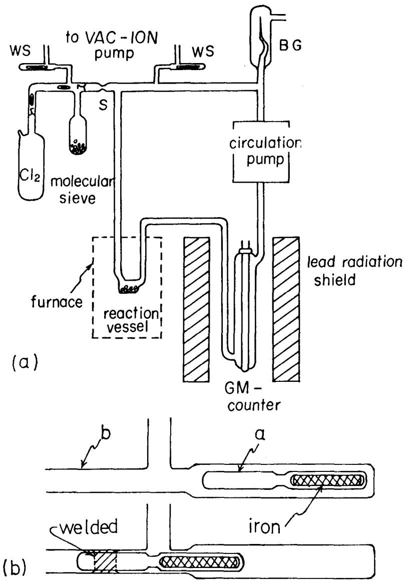

Fig. 1(a). Apparatus for the gas/solid-isotopic exchange reaction. WS, welding seal; BG, Bourdon type vaccuum gauge; S, common type seal.
(b) Detail of welding seal with a high conductance.

The samples were dehydrated by baking at 60—80 °C for 5—10 hr in a vacuum. The temperature was then gradually raised to 200 °C over 3—5 hr and kept at that temperature for 3—7 hr. After pre-baking in a vacuum, the system was sealed off from a diffusion pumping line, thus being made grease free. Further baking-out was carried out with a Vac-Ion pump. The system was isolated when the residual pressure became lower than 5×10^{-7} Torr during the course of baking of the sample at about 350 °C. The sample thus obtained was free from any external contamination of grease and water vapor, and its surface was adequately clean for the present purpose,[7] even though ultra high vacuum (below 10^{-9} Torr) could not be reached. A welding-seal was improved to be less-resistive as shown in Fig. 1 (b). To seal the system, a glass rod *a* is inserted into the outer tube *b* with the aid of magnet, the rod being welded to the outer tube.

First the temperature of the sample was raised to the reaction temperature. Purified chlorine gas was then carefully introduced into the system through a breakable seal and circulated by a circulation pump during the course of reaction. The reaction was followed by counting 0.714 MeV β-ray from ^{36}Cl in the gaseous phase, diffused from the crystallites, with the thin-wall-type GM counter. The temperature of the sample was controlled within 0.2 °C of a preset temperature by the aid of a PID-controller.

Materials Chlorine gas with a nominal purity of 99.8% (contained in a glass cylinder, Takachiho Chemical Co., Ltd.) was distilled and dehydrated with a Linde-3A molecular sieve in a vacuum system. Dehydration of chlorine gas is indispensable.[7]

Radioactive dichlorides were obtained by the isotopic dilution method. Their precipitates were prepared by a modified Marshall's method;[8] *i.e.*, by adding about 100 parts of distilled ethyl ether to one part of a nearly saturated alcoholic solution of the chlorides. Ethyl alcohol used had been dehydrated with a Linde-3A molecular sieve and distilled prior to use. After replacing the supernatant phase with ethyl ether, the precipitates were transferred into the vacuum system together with ethyl ether evaporated in situ. Conditions for preparation and properties of specimens are as follows.

$MgCl_2\cdot6H_2O$ (Merck G.R. reagent, item No. 5833) contains univalent impurities (Na^+ and K^+) nominally amounting to 20 ppm, the specific activity of the resulting radioactive dichloride being about 65 μCi/g. Special care was taken in the treatment of $MgCl_2$ specimens, since the substance is easily splashed by sudden heating in a vacuum and easily turns to magnesium hydroxychloride at 118 °C in air. The crystallites of $MgCl_2$ baked-out in a vacuum had a BET area of about 24 m^2/g.

Cobalt dichloride was prepared by the reaction between cobalt sponge (L. Light Co., Ltd., assay 99.99%) and distilled hydrochloric acid. It contained 20 ppm of sodium as determined by radio-activation analysis, the specific activity being about 5.3 μCi/g. The crystallites of $CoCl_2$ had a BET area of about 6 m^2/g.

Results and Analysis

The diffusion equation by Fick can be solved under the following boundary conditions: 1) the system is homogeneous and isotropic, 2) the initial concentration of radio-tracer is uniform over the crystals, and 3) the ratio of the amount of tracer diffused out (n) to that in the bulk is so small that the model of semi-infinite media can be used. Then n is given as a function of time t:[9]

$$n = (2AN_0)(Dt/\pi)^{1/2}, \tag{1}$$

where A denotes the surface area of specimen, N_0 the initial concentration of the tracer in the crystal, and D the diffusion coefficient. If we denote the counting rate by C, we obtain the following equation as a solution of the diffusion equation.[2,3]

$$C = C_0 + (2AN_0/\alpha\sqrt{\pi})(D_1t_1+D_2t_2+\cdots)^{1/2} \tag{2}$$

or

$$(C-C_0)^2 = (4A^2N_0{}^2/\alpha^2\pi)(D_1t_1+D_2t_2+\cdots) \tag{3}$$

where C_0 denotes the counting rate resulting from ^{36}C, diffused out of the surface region of the crystals, and α the conversion factor between C and n. Suffix i specifies the number of runs carried out successively for a given sample. In real crystals the properties of the surface region differ from those in the bulk, even though the bulk is homogeneous with respect to diffusion.[3,7,10] The diffusion coefficients in the surface region, in general, are much larger than those in the bulk. In the initial stage of the exchange reaction, diffusion from the surface region is observed, and then

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[7] T. Takaishi and Y. Sensui, *Trans. Faraday Soc.*, **63**, 1007 (1967); *Surface Science*, **19**, 339 (1970).

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

[9] S. Chandrasekhar, *Rev. Modern Phys.*, **15**, 1 (1943). A. B. Lidiard and K. Thermalingam, *Discuss. Faraday Soc.*, **28**, 64 (1959).

[10] G. C. Benson, P. I. Freeman, and E. Dempsey, *Adv. Chem. Ser.*, **33**, 26 (1961); *J. Chem. Phys.*, **39**, 302 (1963).

bulk diffusion takes place.[3,7] Such a surface effect is taken into consideration as a correction term C_0 in Eqs. (2) and (3).

If the single path mechanism is applicable, the plots of $(C-C_0)^2$ against time may well be fitted by a straight line, and the Arrhenius plots of D_i may become a linear line.

Magnesium Dichloride. Diffusion experiments were carried out in the temperature range 180—350 °C. The exchange reaction referred to the surface of the crystallites proceeded even at −21 °C as shown in Fig. 2, while the self-diffusion of chloride ions in the bulk did not occur appreciably at temperatures below 180 °C. This indicates that chloride ions much more easily migrate in the surface region of the crystallites than in the bulk and Eqs. (2) or (3) is applicable to the present system. Three samples of magnesium dichloride crystallites were used to check the reproducibility of the data. The total counting rate in the gaseous phase are plotted against the square root of reaction time in Fig. 3(a), which represents an initial stage of the diffusion reaction at 180 °C. Except for the initial portion, the experimental points lie on a straight line, where the bulk diffusion may control the reaction; namely, the results can be well described by Eq. (2). However, there are some ambiguities as to the start of the reaction on the time scale. Measured time t should be replaced by an effective time interval $(t+\delta)$, where the value for δ is determined by the method given previously.[2,3] The abscissa in Fig. 3 is the effective time thus corrected. On the other hand, the intersection of the asymptote with the ordinate

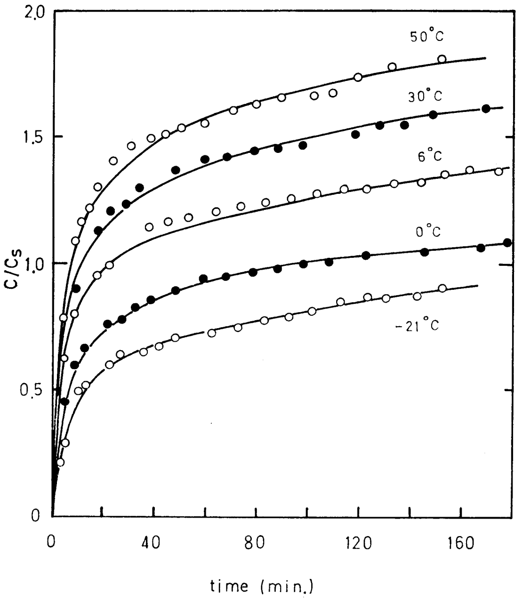

Fig. 2. Plots of counting rate against time in the exchange reaction between Cl_2 and the surface region of $MgCl_2$ crystallites. The value, $C/C_S=1$, corresponds to a monolayer exchange: Solid curves show calculated values based on Eq. (6).

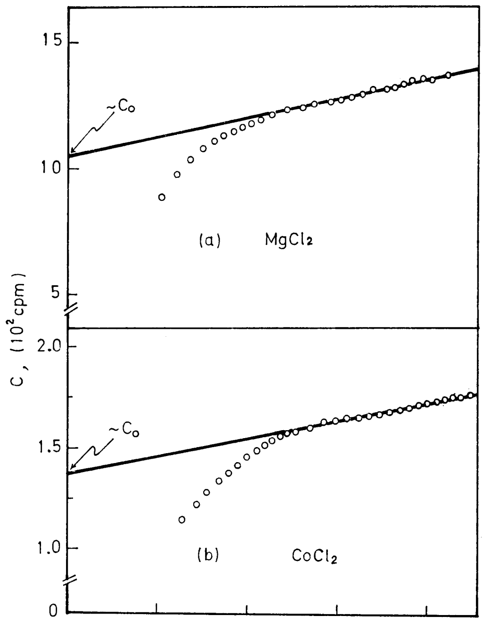

Fig. 3. Plots of C against a square root of time. (a), $MgCl_2$; (b), $CoCl_2$.

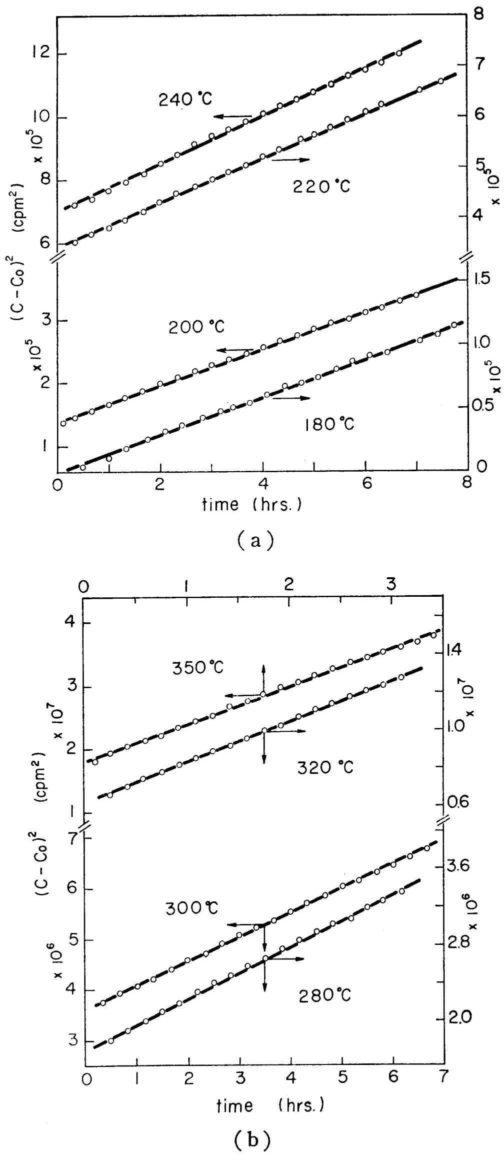

Fig. 4. Plots of $(C-C_0)^2$ against time referred to $MgCl_2$ (Sample No. I).
(a), 180—240 °C; (b), 280—350 °C.

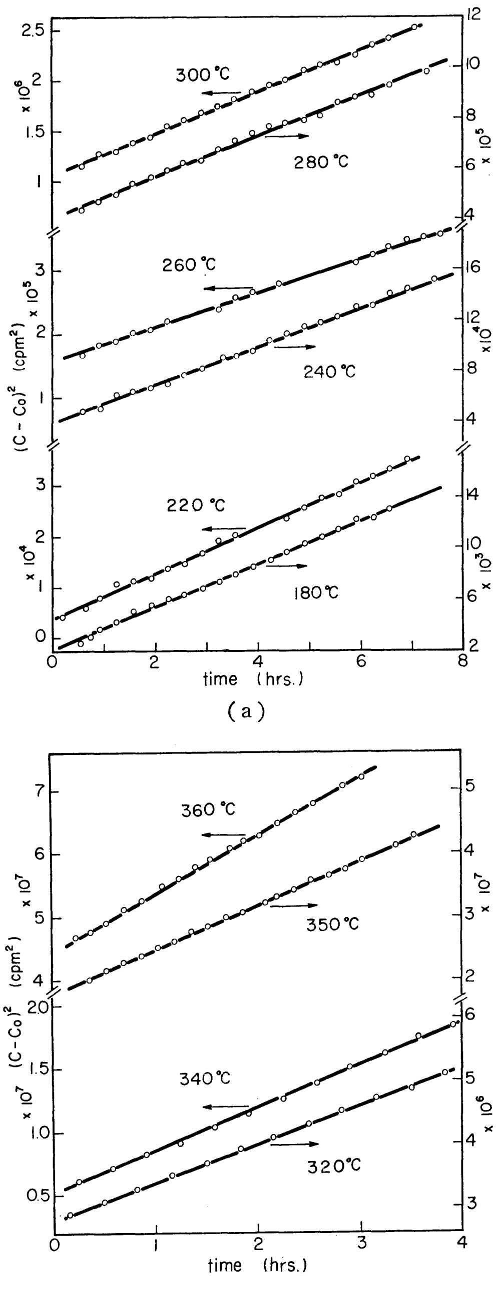

Fig. 5. Plots of $(C-C_0)^2$ against time referred to CoCl$_2$ (Sample No. I).
(a), 180—300 °C; (b), 320—360 °C.

gives a value for C_0. By using C_0-values thus determined, $(C-C_0)^2$ are plotted against time in Fig. 4, in which the points obtained lie on straight lines within experimental error. It is considered that the scattering of the data is mainly attributable to an incomplete mixing of ^{36}Cl in gaseous phase and partly to some drifts in the back-ground-counting rate. From the linear relationship the validity of the homogeneous crystal model may be envisaged. Values for $(4A^2N_0^2/\pi\alpha^2)D$ can be obtained from the slopes of the lines. Arrhenius plots of these values are shown in Fig. 6, in which all the curves consist of two segments of lines with breaks at about 270 °C ($1/T=1.85\times10^{-3}$ K^{-1}) and two kinds of slope are found.

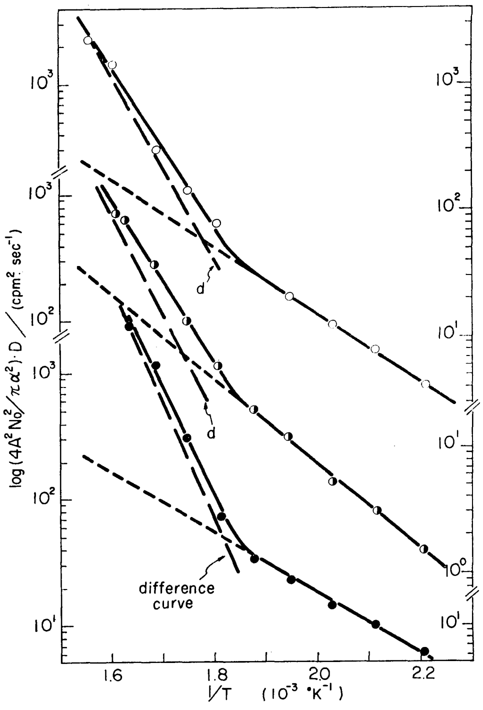

Fig. 6. Arrhenius plots of the apparent diffusion rates in MgCl$_2$.
○, Sample No. I; ◑, No. II; ●, No. III.

In the vacancy diffusion mechanism, the diffusion coefficient D may be expressed as[11]

$$D = D_0(1)\exp[-E/kT] + D_0(2)\exp[-(E+H_v/n_v)/kT] \quad (4)$$

where both $D_0(1)$ and $D_0(2)$ denote terms containing activation entropy and frequency, E is activation energy for the migration of vacancy, and H_v/n_v the apparent heat of the formation per one vacancy. The value for n_v depends on the mechanism of its formation, and we must make a choice between conceivable mechanisms.

If the vacancy mechanism of diffusion can be applied, the slopes in the lower temperature regions give the activation energy for migration of vacancy or Cl$^-$ ions, E. When we plot the difference between the observed curve in the lower one, straight lines are obtained. The value for $(E+H_v/n_v)$ can be determined from the slope of the difference curve as given in Table 1.

Cobalt Dichloride. The temperature range studied was 180—360 °C. It may safely be assumed that chloride ions migrate more easily in the surface region than in the bulk. The total counting rate in the gaseous phase is plotted against the square root of effective time, $(t+\delta)^{1/2}$, in Fig. 3(b). In this case also experimental points lie on a straight line, except for the initial portion; namely, Eq. (2) can be applied to the CoCl$_2$/Cl$_2$ system. By the use of the values for C_0 obtained in Fig. 3(b), $(C-C_0)^2$ are plotted against reaction time in Fig. 5. The experimental points lie on straight lines within experimental error, the homogeneous crystal model thus being also valid in the

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[11] R. A. Swalin, "Thermodynamics of Solids" John Wiley & Sons, Inc., New York, N. Y. (1962).

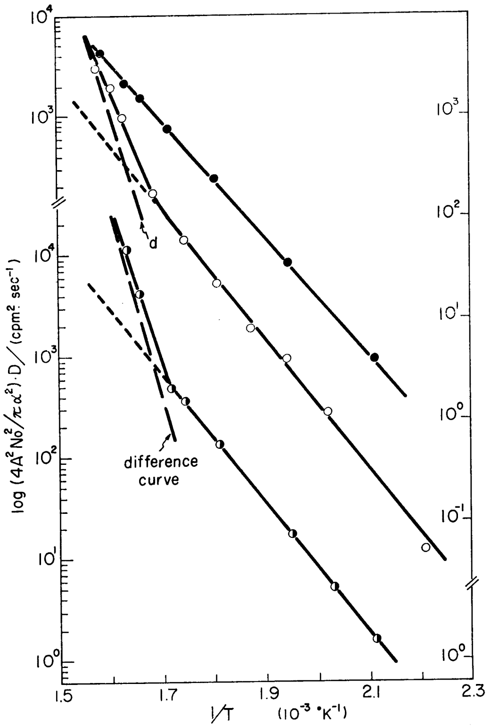

Fig. 7. Arrhenius plots of the apparent diffusion rates in $CoCl_2$.
○, undoped sample (I); ◐, undoped sample (II); ●, sample doped with Na amounting to 250 ppm.

present case. Values for $(4A^2N_0^2/\pi\alpha^2)D$ determined from the slopes of lines are plotted against $1/T$ in Fig. 7. These curves have a similar form to those in Fig. 6, having breaks at about 320 °C ($1/T = 1.7 \times 10^{-3}\ \text{K}^{-1}$). The temperature of the break point is slightly higher than that on $MgCl_2$. The values for E and $(E+H_v/n_v)$ obtained are also given in Table 1.

If monovalent metal ions are doped in crystals of divalent metal dichloride, anion vacancies may be produced to satisfy electrical neutrality conditinon in the crystal. This effect was examined for $CoCl_2$ crystallites doped with sodium, whose concentration was 250 ppm as determined by radioactivation analysis. The same diffusion law was also valid in the doped crystallites. Arrhenius plots of the apparent diffusion coefficient are shown in Fig. 7. We see that the doped crystal has no break in the line in the temperature range studied, while the undoped crystallites containing 20 ppm of sodium have a break. From the slope of the line referring to the doped crystallites, the activation heat was evaluated to be 1.2 eV which is in harmony with E of the undoped crystallites (*cf.* Table 1); namely, the activation heat observed in doped crystallites should be referred to the activation energy for migration of vacancy or Cl^- ion. Thus, the experimental results support the theoretical prediction that the position of break point depends on the content of impurity, and the assumption that the vacancy migration is a dominant mechanism.

Table 1. The values for E and $(E+H_v/n_v)$ in divalent metal dichloride crystallites with $CdCl_2$-type structure

Specimen	E (eV)	$E+H_V/n_V$ (eV)	H_V/n_V (eV)	Remarks
$MgCl_2$ I	0.53	1.4	0.87	Present work
II	0.62	1.6	0.98	
III	0.48	1.8	1.32	
Average	0.55	1.6	1.05	
$CoCl_2$ I	1.3	3.2	1.9	Present work
II	1.25	3.4	2.15	
Average	1.3	3.3	2.0	
$MnCl_2$ I	0.96	2.0	1.04	Previous work²⁾
II	0.92	2.0	1.08	
III	—	2.3	1.4	
IV	—			
Average	0.9	2.1	1.2	
$NiCl_2$ I	1.0^1	—	—	Previous work³⁾
II	1.0^2	—	—	
III	1.0^5	—	—	
Average	1.0			

Discussion

In crystals with the $CdCl_2$-type structure, chlorine atoms are arranged in the cubic closest-packing structure and a metal atom occupies an octahedral hole made of six chlorine atoms, forming a sandwich structure with a layer arrangement ······(Cl–M–Cl)(Cl–M–Cl)······. Since the primary valence of the metal and chlorine atoms are satisfied within each sandwich, the van der Waals force operates between adjacent sandwiches.[13] However, the situation is not so simple; namely, there are two types of layer arrangements in the closest-packing structure, *i.e.*, the cubic type, ······ABC·ABC······, and the hexagonal one, ······AB-ABA······. Choice between the two structures is determined by the magnitude of the interaction between the metal layer and the chlorine layer in the adjacent sandwiches. If the interaction is very weak, the diffusion of Cl^- ions may be highly anisotropic, while, if strong, it approaches an isotropic diffusion. At the present stage of our knowledge on crystal structures, nothing can be predicted as to the magnitude of such interactions. We can only say that the experimental data are well described by a model of isotropic diffusion.

The values for $D_0(1)$ and $D_0(2)$ in Eq. (6) obtained with this model are given in Table 2. Plots of log $D_0(j)$ against the activation heat lie on a straight line as shown in Fig. 8; namely, the theta-rule[12] holds. This means that the method of analysis used is supported.

Table 2. Values for the pre-exponential factors of the apparent diffusion coefficients ($cm^2 \cdot s^{-1}$)

Specimen	$D_0(1)$	$D_0(2)$	Remarks
$MgCl_2$	$(4.5\pm2)\times10^{-13}$	$(5\pm4)\times10^{-3}$	Present work
$CoCl_2$	$(2.5\pm0.5)\times10^{-5}$	2×10^{11}—2×10^{14}	
$MnCl_2$	$(9\pm4)\times10^{-10}$	8 ± 5	Previous work²⁾³⁾
$NiCl_2$	$(3.2\pm0.8)\times10^{-8}$	—	

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12) G. M. Schwab, *Advan. Catal.*, **2**, 251 (1950).

13) A. F. Wells, "Structural Inorganic Chemistry," Oxford Univ. Press, London (1962).

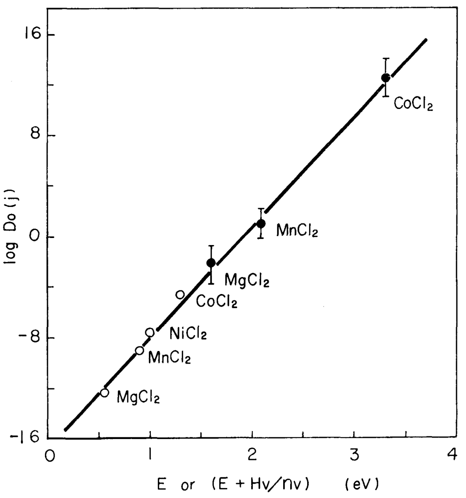

Fig. 8. Linear relationship between log $D_0(j)$ and E or $(E+H_V/n_V)$.
$D_0(j)$ is the pre-exponential factor of diffusion coefficient and given in the unit of cm^2·s^{-1}.
○ and ● refers to E and $(E+H_V/n_V)$, respectively.

According to Benson and his co-workers,[10] the surface of ionic crystal is deformed; namely, anions and cations in the surface region are displaced towards outer and inner directions from ideal lattice points, respectively. Such a distortion may increase the surface reactivity of the crystal. This prediction was proved quantitatively in the case of alkali chloride by Takaishi and Sensui.[7,14] Benson's theory may not be applied to divalent metal chloride crystals without further refinements, since these crystals have partly covalent nature. However, we can expect qualitatively that the surface region has different properties from the bulk, and ions in the surface region can migrate more easily than in the bulk. This prediction was semi-quantitatively proved in NiCl$_2$ crystallites.[3] Let us analyze the data on MgCl$_2$ to verify the prediction.

It may be safely assumed that there are two domains in the first layer of the crystal surface and that the distortion in the first layer influences the configuration of the second layer. The reverse reaction from the gaseous phase to the solid is ignored due to the boundary condition mentioned above, the kinetic equation being given by[3]

$$\begin{aligned}
dn_g(i)/dt &= k_1(i)n_1(i)\\
dn_1(i)/dt &= -\ k_1(i)n_1(i)\ -\ k_2(i)n_1(i)\ +\ k_2(i)n_2(i)\\
dn_2(i)/dt &= -\ k_2(i)n_2(i)\ +\ k_2(i)n_1(i)\ -\ k_3n_2(i)\ +\ k_3n_3(i)\\
n(i)\ +\ n_1(i)\ &+\ n_2(i)\ +\ n_3(i)\ =\ 3a(i), \qquad (5)
\end{aligned}$$

and

$$n_g=\sum_{i=1}^{2}n_g(i),\quad n_1=\sum_{i=1}^{2}n_1(i),\quad n_2=\sum_{i=1}^{2}n_2(i),\quad n_3=\sum_{i=1}^{2}n_3(i),$$
$$a=\sum_{i=1}^{2}a(i),$$

where n_i denotes the number of ^{36}Cl in the i-th layer at time t; a, the number of ^{36}Cl contained in each layer at $t=0$; k_j, the apparent rate constant of the exchange reaction between the $(j-1)$th and the j-th layers; subscript g, the gaseous phase; and (i), the i-th kind of domain. In Eq. (5) it is assumed that $k_3(1)$ and $k_3(2)$ have the same value, k_3. If ^{36}Cl in gaseous phase amounting to a results in a counting rate C_s, it can be expressed as $C_s=\alpha\cdot a$ and $C/C_s=n_g/a$. Then, the solution of Eq. (1) is expressed[3] as

$$\begin{aligned}
\frac{C(i)}{C_s(i)}=\frac{n_g(i)}{a(i)}&=\frac{k_1(i)}{\rho_+(i)\rho_-(i)}\left\{\frac{k_2(i)k_3}{\lambda}-\rho_+(i)-\rho_-(i)-k_1(i)\right\}\\
&-\frac{k_1(i)k_2(i)k_3}{\lambda[\lambda+\rho_+(i)][\lambda+\rho_-(i)]}\exp(-\lambda t)\\
&-\frac{k_1(i)}{\rho_+(i)[\rho_+(i)-\rho_-(i)]}\left\{\rho_-(i)+k_1(i)\right.\\
&\left.-\frac{k_2(i)k_3}{\lambda+\rho_+(i)}\right\}\exp[\rho_+(i)t]\\
&-\frac{k_1(i)}{\rho_-(i)[\rho_-(i)-\rho_+(i)]}\left\{\rho_+(i)+k_1(i)\right.\\
&\left.-\frac{k_2(i)k_3}{\lambda+\rho_+(i)}\right\}\exp[\rho_-(i)t]
\end{aligned}$$

with

$$\begin{aligned}
2\rho_\pm &= -[k_1(i)+2k_2(i)+k_3]\\
&\mp[k_1(i)^2+4k_2(i)^2+k_3{}^2-2k_1(i)k_3]^{1/2} \qquad (6)
\end{aligned}$$

where λ denotes an effective rate constant for the decrease in n_3. By a comparison of Eq. (5) with the experimental curves, the best-fitting values for k_1(i), k_2(i) and k_3 are determined with the aid of an electronic computer. The results are well described by the theory, as shown in Fig. 2. The Arrhenius plots of $k_1(i)$ and $k_2(i)$ are given in Fig. 9; the activation energies for the exchange reaction are obtained to be: 3.4 kcal/mol (=0.15 eV) for the active part of the first layer, 7 kcal/mol (=0.3 eV) for the less-active one, 10 kcal/

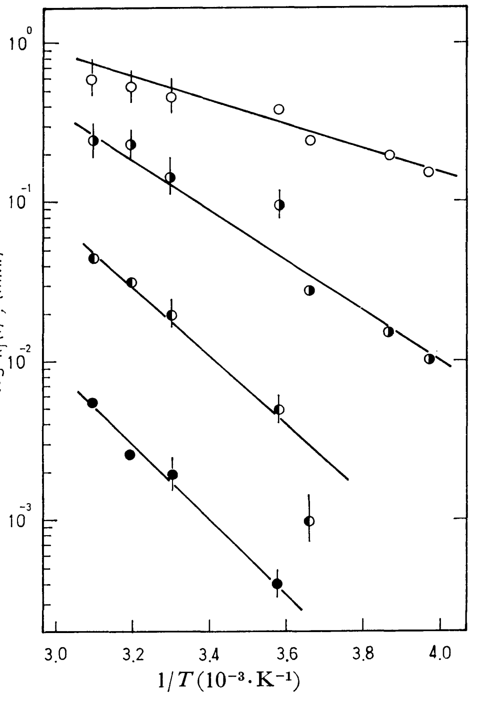

Fig. 9. Arrhenius plots of the rate constants for the exchange reaction in the surface region of MgCl$_2$ crystallites.
○, active domain in the first layer; ◑, less-active domain in the first layer; ◐, active domain in the second layer; ●, less-active domain in the second layer.

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[14] T. Takaishi and Y. Sensui, *Trans. Faraday Soc.*, **65**, 131 (1969).

mol (=0.43 eV) for the active part of the second layer, and 11 kcal/mol (=0.48 eV) for the less-active one. The activation energies of the exchange reaction converge to that of the self-diffusion more rapidly in $MgCl_2$ than in $NiCl_2$. This conclusion is semi-quantitative, since the present data on $MgCl_2$ are less quantitative. In $MnCl_2$ and $CoCl_2$, such a surface effect was observed only qualitatively but distinctly. Thus, we can say that high reactivity of the surface is a fairly common phenomenon which may be of value for further studies in connection with catalytic properties.

The value for n_v in Eq. (4) could not be determined. However, Simkovich[15] studied the mechanism of electrical properties and arrived at the conclusion that the associated vacancy is dominantly formed as

$$0 \rightarrow (V_{Pb}V_{Cl})' + V_{Cl}' + H_v$$

where V_x' denotes the vacancy of x atom (or ion). It may generally be considered that vacancies with effective charge, 2e, are rather unstable electrostatically and apt to form associated vacancies. If so, we may apply the above mechanism to other MeX_2 crystals; namely, $n_v=2$ may be presumed.

The author would like to express his gratitude to Prof. Tetsuo Takaishi, Rikkyo University, for valuable suggestions.

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[15] G. Simkovich, *J. Phys. Chem. Solids.*, **24**, 213 (1963).