DIFFUSION OF Zn AND Cd IN SODIUM CHLORIDE SINGLE CRYSTALS*

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ABSTRACT: The diffusion coefficient of divalent zinc and divalent cadmium in sodium chloride single crystals grown from the melt was determined by atomic absorption spectrophotometry. The diffusions were made over the temperature range from 540 °C to 720 °C for zinc and from 530 °C to 655 °C for cadmium. The diffusion coefficient of zinc in sodium chloride was $D = 4.0 \times 10^{-2} \exp(-1.06/kT)$; and the corresponding one for cadmium: $D = 3.9 \times 10^{-3} \exp(-0.26/kT)$.

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INTRODUCTION

Different methods have been used to measure the rate of diffusion of divalent impurities in single crystals of sodium chloride as a function of temperature. The method of radioactive tracers has been used by S. J. Rothman et al[1] to determine the diffusion of zinc into NaCl crystals. For cadmium in NaCl, T. Ikeda[2] used a method based upon the observation of a difference in colloidal coloration between pure and impure regions of the NaCl crystal.

In this work atomic absorption spectrophotometry is used to determine the diffusion coefficient of zinc and cadmium in sodium chloride single crystals. This method of analysis was selected in view of the advantages it presents. Among these advantages we can mention its high sensibility and precision.

The experiments reported in this work are such that the diffusion changes only along the thickness of the crystal, so we can consider it as a one-dimensional flow, and under this assumption the solution to Fick's second law is the thin film solution[3]. From it, the diffusion coefficient at a particular temperature and time can be determined:

$$C = \frac{C_0}{(\pi D t)^{\frac{1}{2}}} \exp\left(- \frac{x^2}{4Dt}\right).$$

C_0 is the initial amount of solute deposited on a face of the sample, t the time, and x the distance measured from the surface of the sample. The diffusion coefficient changes exponentially with temperature according to the equation[3]

$$D = D_0 \exp(-E/\mathrm{kT})$$

where D_0 is the diffusion pre-exponential factor and E the activation energy for diffusion.

EXPERIMENTAL

The method of Kyropoulos in the open atmosphere[4] (with some modifications[5]) was used to grow the single crystals using 250 grs. of sodium chloride of reagent grade (J. T. Baker Chemical Co.). The samples to be used in the experiments were cleaved from a crystal into slices of the required dimensions ($15 \times 15 \times 8$ mm^3). Saturated solutions of zinc chloride and cadmium chloride in ethyl alcohol were prepared and deposited upon one face of each sample; after this procedure, the sample was transfered, to a constant temperature furnace in which the diffusion proceeded for a known time. The diffusion time was in the range between 14.4×10^3 sec. and 100.8×10^3 sec. for zinc, and between 43.0×10^3 sec. and 115.0×10^3 sec. for cadmium. Similar samples were mounted one against the other, to avoid the evaporation loss of the impurity. The annealing temperatures were measured with an iron-constantan thermocouple. Next, the samples were sectioned with a microtome with a sectioning thickness of 100μ. From each crystal we get about fifteen samples for the impurity concentration analysis. The analysis was done with a Perkin-Elmer, Model 303 atomic absorption spectrophotometer.

RESULTS AND CONCLUSIONS

Temperature variations of the diffusion coefficients are shown in figure 1. The values of the diffusion pre-exponential factor and of the activation energy for zinc and cadmium in NaCl are shown in Table I. The error in activation energies were estimated to be of 10%.

TABLE I

Impurity	Temperature range	Other Authors		This work	
		$D_0\,(cm^2/sec)$	E (ev)	$D_0\,(cm^2/sec)$	E (ev)
Zn^{2+}	540°C–720°C	2.0×10^{-2}	1.02[1]	4.0×10^{-2}	1.06
Cd^{2+}	530°C–655°C	3.0×10^{-3}	0.21[2*]	3.9×10^{-3}	0.26

* Diffusion parameters calculated from the graph of temperature variations of the diffusion coefficient given in that reference.

From Table I, one can see that the results obtained show a very good agreement with those of the authors cited and, in view of the greater sensibility and accuracy of the method we used, we think that our results are more reliable.

It was considered of interest to measure the background impurity content in the crystals used in this work. For this purpose the crystals were analyzed

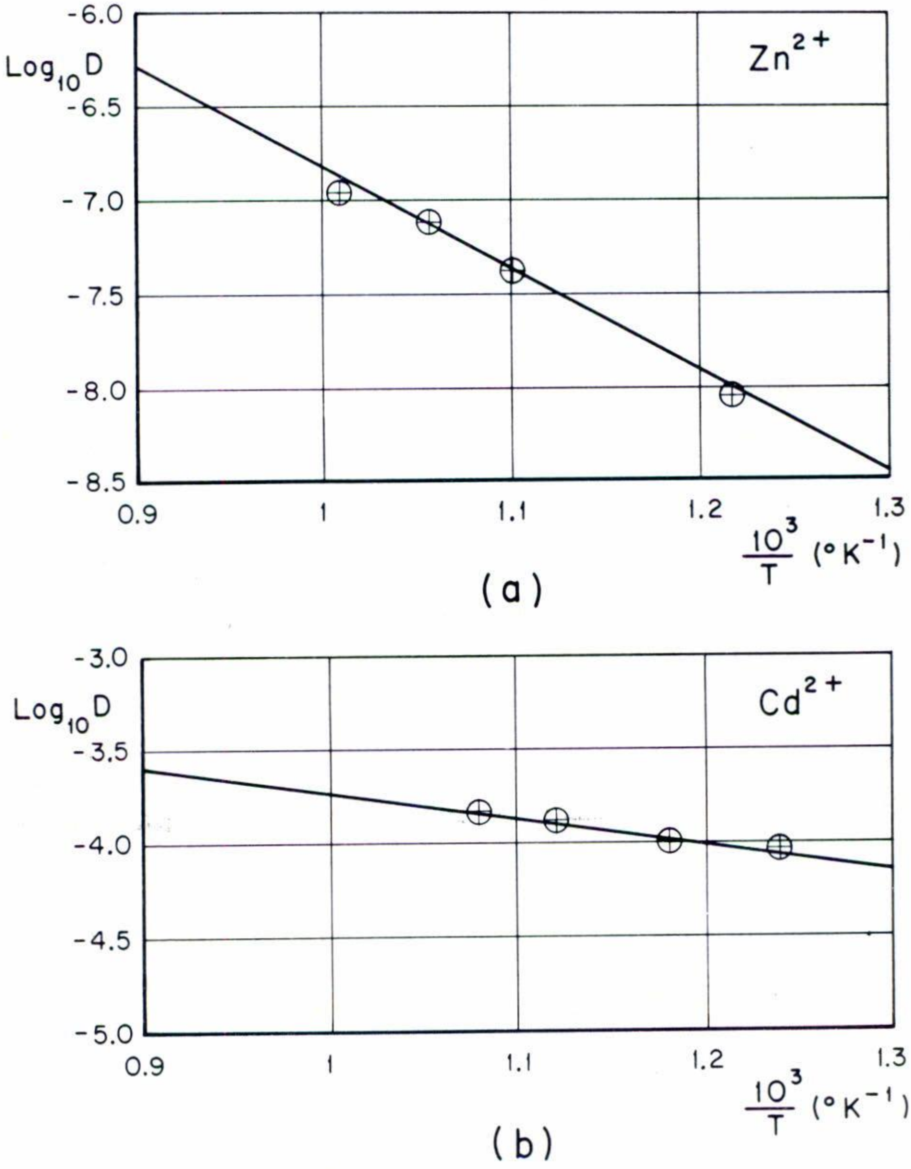

Fig. 1. Temperature variations of the diffusion coefficient, for Zn^{2+}(a) and for Cd^{2+}(b).

using emission spectrography and atomic absorption spectrophotometry[6], finding Fe, Mg, Ca and Ba in orders of 10^{-3} wt.%. Although these orders are small, it is necessary to know the valence of the impurity to conclude something about their possible contribution to the vacancy concentration.

REFERENCES

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RESUMEN

Utilizando espectrofotmetría por absorción atómica se determina el coeficiente de difusión de Zn^{2+} y Cd^{2+} en monocristales de NaCl crecidos a partir del fundente. Las difusiones se realizaron en los intervalos de temperatura de 540°C a 720°C para el zinc, y de 530°C a 655°C para el cadmio. Los coeficientes de difusión se determinaron a partir de la ecuación $D = D_0 \exp(-E/kT)$; los valores encontrados para los parámetros fueron: $D_0 = 4.0 \times 10^{-2}$ cm^2/seg. y $E = 1.06$ ev para el zinc; y $D_0 = 3.9 \times 10^{-3}$ cm^2/seg y $E = 0.26$ ev para el cadmio.