Fyzikálny časopis 18 (1968), No. 4

SOLUBILITY OF FREE Cd^{++} IN NaCl CRYSTALS

VIERA TRNOVCOVÁ, Bratislava

INTRODUCTION

Available data on the solubility of divalent cation admixtures in NaCl crystals are rather scanty and predominantly of a qualitative character. Information on the temperature dependences of solubility enables us to develop further the theory cf solubility and provides values of heats of solution. They are moreover of primary importance for interpreting experiments of various types. They help to decide definitely whether the results of the experiments are influenced by precipitation.

A simple theory of solubility of divalent admixtures in ionic crystals has been presented by Lidiard [1]. Haven [2] has proposed an experimental method of determining the solubility of a free divalent admixture in alkali halides by measuring the temperature dependence of the ionic conductivity in doped crystals. Using this method he determined the solubility of free Mn^{++}, Cd^{++} and Ca^{++} [3] in NaCl within the temperature range of 200 °C to 400 °C as well as the corresponding heats of solution. Using the same method, Rothman et al. [4] followed the solubility and the heat of solution of free Zn^{++} in NaCl crystals, while the solubility and heats of solution of free Ba^{++} and Sr^{++} were investigated by Brown et al. [5]. As for Zn^{++}, the temperature dependence of the total solubility determined by the method of diffusion saturation is also known [6].

The suitable form of temperature dependences of ionic conductivity in NaCl + $CdCl_2$ crystals has made possible to determine the temperature dependence of solubility of free Cd^{++} and the corresponding heat of solution by the conventional method of conductivity measurements [2]. This admixture has been studied because it is frequently used in NaCl, owing to its ionic radius approaching that of Na^+ and because the earlier measured temperature dependence of its solubility is rather questionable [3]. It leads namely to a higher solubility of Cd^{++} than that of Ca^{++} in NaCl above 300 °C, which contradicts the observations.

EXPERIMENTAL

The NaCl single crystals were grown in a protective atmosphere by the Kyropoulos method. The *dc* conductivity was measured on samples provided with electrodes by applying a thin coating of alcoholdag. The samples were clamped between two massive Ni-electrodes, the temperature of which was determined to an accuracy of ±1 °C by means of Pt-PtRh thermocouples. Measurements were carried out in a dry Ar atmosphere. The concentration of cadmium in samples was determined by spectral emission analysis. Ni in a concentration of 5×10^{-3} was used as the internal standard and the intensity of 3417.77 Å (Ni) and 3261.06 Å (Cd) lines was measured.

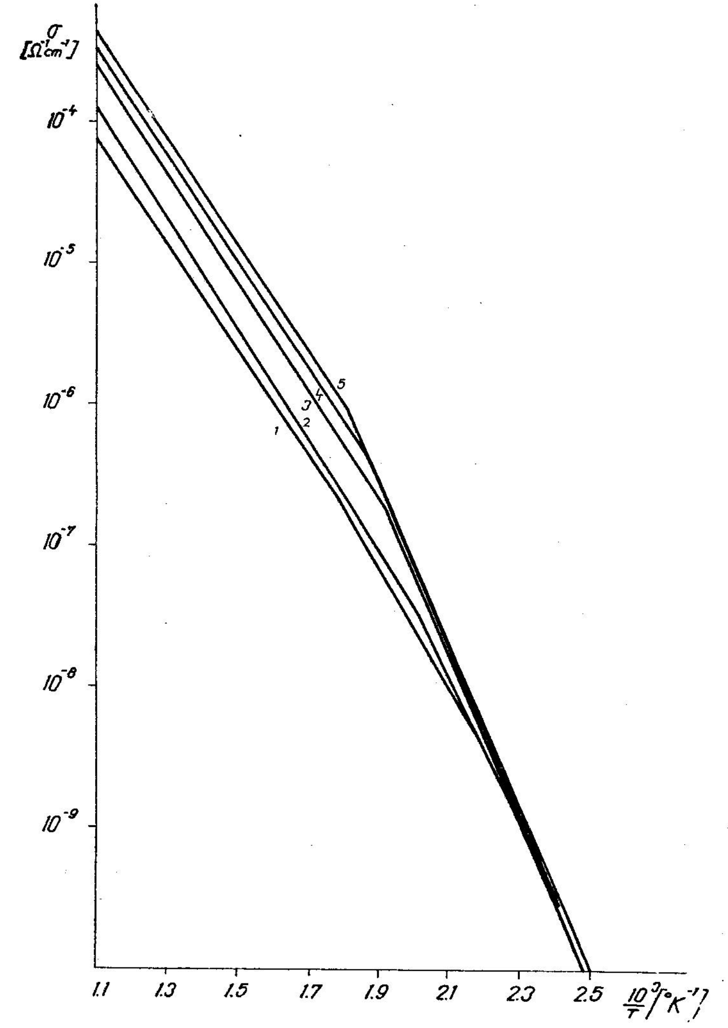

Fig. 1. Temperature dependences of the conductivity of NaCl + $CdCl_2$ crystals with different concentrations of $CdCl_2$: 1. 1×10^{-2} mo—% Cd^{++}; 2. 1.6×10^{-2} mol—% Cd^{++}; 3. 3.4×10^{-2} mol—% Cd^{++}; 4. 4.2×10^{-2} mol—% Cd^{++}M 5. 5.2×10^{-2} mol—% Cd^{++}.

RESULTS

The temperature dependence of the ionic conductivity in NaCl + $CdCl_2$ crystals has been measured over the temperature range 150—630 °C and over the concentration range of 1×10^{-2}—6×10^{-2} mole-% Cd^{++}. Some of these dependences measured are shown in the form of $\ln \sigma$ against $1/T$ plots in Fig. 1, where T stands for absolute temperature, while σ is ionic conductivity. The effect of precipitation of admixtures was easily recognized on these dependences by a sharp *break* and an independence of conductivity on the increasing concentration of admixture at a temperature lower than that of the *break*. In equilibrium the conductivity of a crystal in the precipitation region should depend only on the temperature and the kind of admixture. The dependences shown in Fig. 1 were measured by heating the crystals; they correspond to the equilibrium. At temperatures above that of the *break* the impurity-induced free vacancy region, i. e. the so-called impurity region, can be distinguished. The transitional impurity-vacancy association region is appreciable only at the lowest concentrations of the admixture.

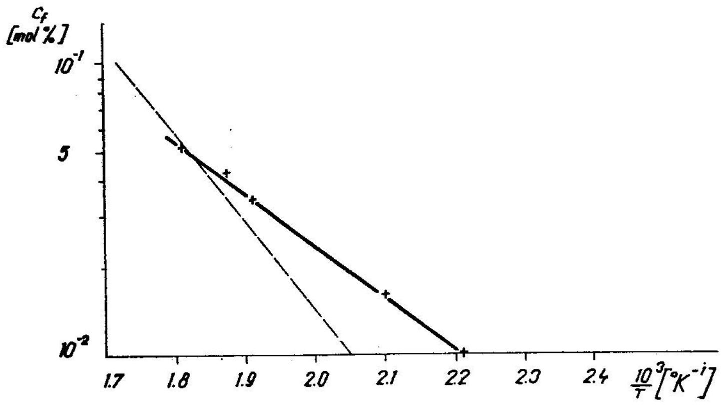

Fig. 2. Temperature dependence of the solubility of free Cd^{++} in NaCl (dashed line — dependence determined by Haven [3]).

By extrapolation of the impurity region to the precipitation region the free-impurity solubility *break* temperature was obtained. We considered this temperature to be the temperature at which the concentration of free admixture, equalling that determined by chemical analysis, would reach the limit of solubility. Using Haven's method [2] we determined the temperature dependence of the solubility of free Cd^{++} from the dependence of this *break* temperature on the concentration of Cd^{++}. This dependence together with that obtained earlier by Haven [3] is shown in Fig. 2. In agreement with the simple theory of solubility [1] this dependence is linear, plotting $\ln c_f$ against $1/T$ (c_f being the limit of solubility of free cadmium at temperature T). The least squares method gave the following equation for the solubility of free Cd^{++}

$$c_f = .88 \exp(-\ .355/kT). \qquad (1)$$

DISCUSSION

In order to preserve the condition of electro-neutrality during the process of solution, one cation vacancy $\boxed{+}$ must be formed for every dissolved Cd^{++} ion. Therefore the following relationship holds good

$$\mathrm{CdCl_2}\ \text{(precipitated)} \rightleftarrows \mathrm{Cd^{++}} + \boxed{+} + 2\,\mathrm{Cl^-} - G_i \qquad (2)$$

where $G_i = H_i - TS_i$ is the Gibbs free energy of solution (not including configurational entropy), H_i is the enthalpy (heat) and S_i the entropy of solution per molecule. The following holds for processes of solution of this type [1, 7]

$$c_f \,.\, x_1 = \exp(S_i/k) \exp(-\ H_i/kT) \qquad (3)$$

where c_f and x_1 are the mole fractions of free Cd^{++} and of free cation vacancies, respectively, at the limit of solubility at temperature T. Within our experimental range of temperatures, where the production of thermal vacancies can be neglected, the condition of electroneutrality requires $c_f = x_1$, hence

$$c_f = \exp(S_i/2k) \exp(-\ H_i/2kT). \qquad (4)$$

This type of temperature dependence of solubility may be expected when determining the solubility of free admixtures by means of conductivity measurements. The heat of solution H_i is determined from the slope of the linear dependence of $\ln c_f$ on $1/T$.

The relation (1) obtained for the temperature dependence of solubility of Cd^{++} in NaCl has the form of equation (4), as predicted by theory. It gives the value of .71 eV for the heat of solution of Cd^{++} in NaCl in the temperature range of 200 °C to 400 °C.

Experimentally determined values of heats of solution for various divalent cation admixtures in NaCl, reported by different authors, are compared in Table 1. Since the solubility seems to decrease and the heat of solution seems to increase with the growing difference between ionic radii of the admixture and of Na$^+$, Goldschmidt's ionic radius for each admixture is also given.

Table 1

Experimentally determined values H_i of heats of solution for divalent cation admixtures in NaCl

Admixture	Ionic radius [Å]	H_i [eV]	Reference	Experimental range of temperatures [°C]
Zn^{++}	.83	.92	[6]	350—770
		.98	[4]	410—560
Mn^{++}	.91	.88	[3]	200—400
Cd^{++}	1.03	1.24	[3]	200—400
		.71	present paper	200—400
Ca^{++}	1.06	.64	[3]	200—400
Sr^{++}	1.27	1.80	[5]	320—500
Ba^{++}	1.43	2.00	[5]	470—680

Ca^{++} and Cd^{++} are dimensionally very appropriate and consequently their heats of solution should be low and fairly close to each other. The heat of solution of Cd^{++} determined by us agrees well with this assumption. The reported solubility of Cd^{++} (equation (1)) is lower than the solubility of Ca^{+} [3], in agreement with the findings of various types of experiments within the above-mentioned temperature range. The low solubility of Cd^{++} can be explained by the very low entropy of solution of this admixture.

CONCLUSION

The temperature dependence of the solubility of free Cd^{++} in NaCl crystals has been determined over the temperature range of 200—400 °C by measuring the ionic conductivity of NaCl + CdCl$_2$ crystals. In agreement with the simple theory of solubility [1], this dependence may well be expressed by the equation

$$c_f = .88 \exp(-\ .355/kT).$$

The low value of .71 eV for the heat of solution is caused by the negligible difference between ionic radii of Cd^{++} and Na^{+}. The low solubility of Cd^{++} in NaCl can be explained by the extremely low entropy of solution.

REFERENCES

[1] Lidiard A. B., *Handbuch der Physik*, Bd 20/II. Springer Verlag, Berlin 1957.
[2] Haven Y., Rec. Trav. Chim. (Pays-Bas) *69* (1950), 1505.
[3] Haven Y., *Rep. of the Conf. on Defects in Cryst. Solids.* Bristol 1954, 261.
[4] Rothman S. J., Barr L. W., Rowe A. H., Selwood P. G., Phil. Mag. *14* (1966), 501.
[5] Brown N., Hoodless I. M., J. Phys. Chem. Solids *28* (1967), 2297.
[6] Paulíny-Tóthová V., Popeliš I., Cz. J. Phys. *B* 15 (1965), 921.
[7] Lidiard A. B., J. Appl. Phys. Suppl. *33* (1962), 414.

Received March 15 th, 1968

Fyzikálny ústav SAV.
Bratislava