

ELECTROLYTIC CONDUCTIVITY OF POLAR CRYSTALS WITH BUILT-IN DIVALENT CATION AND ANION ADMIXTURES

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INTRODUCTION

In the past few years several authors began to study anion doped alkali-halides. Pashkovskij, Tsai and Tkatchuk [1] found that the conductivity of $\text{NaCl} : \text{Na}_2\text{CO}_3$ decreases first with an increasing Na_2CO_3 content, but if a certain concentration of the admixtures is surpassed the conductivity increases again with a still further increase of the concentration. This result was confirmed by Kessler and Mariani [2] who pointed out that the excess charge due to the built-in CO_3^{2-} could explain the observed facts if the inherent divalent cation impurities are taken into account. It should be noted, though, that also $\text{NaCl} : \text{NaOH}$ exhibits this characteristic (cf. [2]) and so does obviously $\text{KCl} : \text{KOH}$ (cf. Fig. 9, [3]). Gruzenksy and Scott [4], who studied $\text{KCl} : \text{K}_2\text{SO}_4$, found on the other hand clear evidence of a reaction taking place in the crystal, most probably between divalent cation impurities and between the built-in SO_4^{2-} . By a similar reaction Kessler and Mariani [5] recently could explain quantitatively the conductivity of $\text{NaCl} : \text{CaCl}_2 + \text{NaOH}$. Redfern and Pratt [6] observed only a conductivity decrease if NaCl was doped with divalent anions. Finally Rolfe [7] found the conductivity of $\text{KCl} : \text{K}_2\text{CO}_3$ to be quantitatively consistent with the assumption that in consequence of the built-in anions a negative excess charge is built up. These results do not seem to give a unique picture, it is true, but there are nevertheless certain common features and in the case of $\text{KCl} : \text{K}_2\text{CO}_3$ the simple theory of Stasiv and Teltov [8] (see also Lidiard [12], 285) could satisfactorily explain the observed facts.

We shall therefore try to extend this theory so as to account for simultaneous built-in divalent cation and anion impurities, to find whether the observed facts could be explained by the simultaneous building-in of both kind of impurities. There are certain facts namely, which support such a hypothesis. It is well known that so called *pure* crystals, i. e. undoped ones, contain even if grown from p. a. materials still a considerable quantity of divalent

impurities. This can be confirmed from figures given by Rothman et al. [9], by Gründig and Wassermann [10] and by others. If under these conditions the crystals are doped by anions, they must contain in fact anions as well as cations. Thereby the solubility of the anions is mostly very low.

It is often supposed that in consequence of an addition of anions into the melt when crystals are grown a reaction takes place between both kinds of admixtures resulting in an insoluble compound and that in consequence the crystals should not contain any cation admixtures. But this has not been found to be true. It was found [2] that heavily doped NaCl : NaOH crystals exhibit in consequence of precipitation of the built-in OH⁻ after three quarters of a year the conductivity of an undoped crystal, grown from the same raw material and the reaction yield of the reaction between CaCl₂ (the principal divalent cation impurity [10, 11]) and NaOH in the melt [5] is because of a low concentration of one of the reagents negligible.

Under these circumstances it seems to us useful to investigate the conductivity which might be expected from the theoretical point of view in case of the building-in of both kinds of admixtures and to compare it with the experimental findings.

THE DEPENDENCE OF THE VACANCY CONCENTRATION ON THE DIVALENT CATION AND ANION ADMIXTURES CONCENTRATION

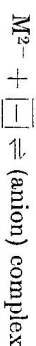
The first step towards our discussion is the determination of the expected defect concentration. We shall consider Schottky-defects only, but for Frankel- or Lidiard [12] § 30: 1) By the solubility product of the cation and anion vacancies

$$x_1 \cdot x_2 = K_{12}^{-1} \equiv x_0^2, \quad (1)$$

where x_1, x_2 denote the respective vacancy concentrations. 2) By the formation of divalent admixture-vacancy complexes, which we suppose occur both with cations and anions and which is governed by the mass action laws

$$\frac{c_1 p_1}{x_1 c_1 (1 - p_1)} = K_1(T); \quad \frac{c_2 p_2}{x_2 c_2 (1 - p_2)} = K_2(T). \quad (2a, b)$$

c_1 and c_2 denote the molar fractions of substitutional built-in divalent cation and anion admixtures, p_1 and p_2 the respective degrees of association. K_1 and K_2 are the mass action constants of the quasi-chemical reactions



which as shown by Lidiard [13] are in case of NaCl-type crystals

$$K = 12 \exp(U_A/kT),$$

U_A is the Gibbs free energy of association. This expression is valid as long as the concentration of the divalent admixtures is not too high. 3) Finally the defect concentration depends on the condition of electroneutrality, i. e. in our case

$$x_1 - x_2 = c_1 (1 - p_1) - c_2 (1 - p_2). \quad (3)$$

If we substitute from (2a) and (2b) into Eq. (3) and introduce, proceeding from (1)

$$\xi = x_1/x_0 = x_0/x_2$$

we get

$$\frac{c_1}{x_0} \cdot \frac{1}{1 + H_1 \xi} - \frac{c_2}{x_0} \cdot \frac{1}{1 + H_2/\xi} = (\xi - 1/\xi) \quad (4)$$

where $H_1 = x_0 K_1$ and $H_2 = x_0 K_2$.

The interpretation of Eq. (4) is simple. Both expressions on the left side represent the admixture concentrations relative to the intrinsic vacancy concentration reduced in accord with the association. It follows from (4) that ξ is steadily increasing with an increasing c_1 , and decreasing with an increasing c_2 . For $c_2 = 0$ Eq. (4) becomes naturally identical with the respective expression found e. g. in Lidiard [12] pg. 301, for the divalent cation admixture induced defect concentration. For $c_1 = 0$ we get the respective expression for the divalent anion admixture induced defect concentration. Finally, if the association is neglected, i. e. $H_1 = H_2 = 0$ we get

$$\xi = \frac{c_1 - c_2}{2x_0} \left\{ 1 + \left(1 + \frac{4x_0^2}{(c_1 - c_2)^2} \right)^{1/2} \right\}, \quad c_1 > c_2 \quad (5a)$$

$$\frac{1}{\xi} = \frac{c_2 - c_1}{2x_0} \left\{ 1 + \left(1 + \frac{4x_0^2}{(c_2 - c_1)^2} \right)^{1/2} \right\}, \quad c_2 > c_1. \quad (5b)$$

If we multiply by x_0 we get x_1 and x_2 , resp.

It is to note that the increase of ξ with c_1 is moderated not only by the increasing cation association, but also in dependence on c_2 and H_2 . The value of $(1 + H_2/\xi)$ decreases namely by an increasing c_1 . Hence the influence of c_2 is enhanced by an increasing c_1 .

The decrease of ξ by an increasing c_2 is moderated at higher c_2 also because the value of $(1 + H_1 \xi)$ in principle decreases. These results are demonstrated in Fig. 1a and 1b.

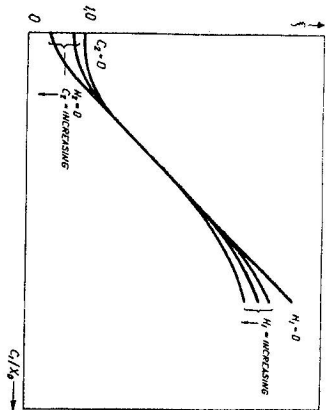


Fig. 1a. The value of ξ in dependence on the cation concentration.

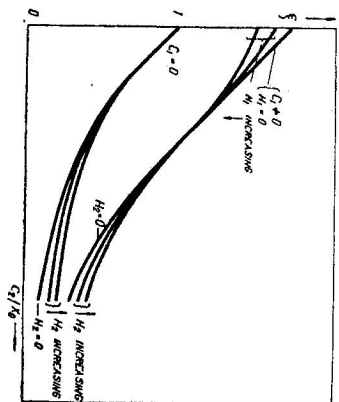


Fig. 1b. The value of ξ in dependence on the anion concentration.

ELECTROLYTIC CONDUCTIVITY

In consequence of the formation of vacancies a charge transport occurs if a voltage-drop is applied on the crystal. If the mobility of the cations is denoted by μ_1 that of the anions by μ_2 the conductivity is $\sigma = eN(x_1\mu_1 + x_2\mu_2)$, where N is the number of molecules per unit volume and e answers the ion charge. It is convenient to discuss instead of σ its ratio to the intrinsic conductivity $\sigma_0 = eNz_0(\mu_1 + \mu_2)$, namely σ/σ_0 . This ratio is found if we use ξ and $\varphi = \mu_2/\mu_1$ to be very simple

$$\frac{\sigma}{\sigma_0} = \frac{\xi + \varphi/\xi}{1 + \varphi}. \quad (6)$$

As mentioned, the value of ξ changes monotonously with c_1 and c_2 . But the dependence of σ/σ_0 on ξ exhibits a minimum

$$\left(\frac{\sigma}{\sigma_0}\right)_{\min} = \frac{2\sqrt{\varphi}}{1 + \varphi}; \quad \xi_{\min} = \sqrt{\varphi}. \quad (7a, b)$$

Therefore it follows that for $\varphi \gg 1$ a minimum is found at $\xi \approx 1$. The value $(\sigma/\sigma_0)_{\min}$ will be < 1 for $\varphi \neq 1$ and equal to 1 for $\varphi = 1$. For a given c_1 , the minimum will be found for

$$c_{2\min} = \frac{1 + H_2\sqrt{\varphi}}{1 + H_1\sqrt{\varphi}} c_1 + x_0 \left(\frac{1}{\sqrt{\varphi}} - \sqrt{\varphi} + \frac{H_2}{\sqrt{\varphi}} - H_2 \right) \quad (7c)$$

and vice versa for a given c_2

$$c_{1\min} = \frac{1 + H_1\sqrt{\varphi}}{1 + H_2\sqrt{\varphi}} c_2 + x_0 \left(\sqrt{\varphi} - \frac{1}{\sqrt{\varphi}} + H_1\varphi - H_1 \right). \quad (7d)$$

If $\varphi \ll 1$ and H_1 is small, so that $H_1\sqrt{\varphi} \ll 1$, Eq. (7c) and (7d) simplify to

$$c_{2\min} \approx (1 - H_2\sqrt{\varphi})(c_1 + x_0/\sqrt{\varphi})$$

$$c_{1\min} \approx c_2(1 + H_2\sqrt{\varphi}) - x_0/\sqrt{\varphi}.$$

With an increasing $H_2\sqrt{\varphi}$ the minimum shifts from $c_2 = c_1$ to higher concentrations of c_2 . At a high enough temperature this shift might be enhanced by thermal vacancies.

Finally we shall establish the transport numbers

$$t_+ = \frac{\sigma_+}{\sigma} = \frac{eN x_1 \mu_1}{eN(x_1 \mu_1 + x_2 \mu_2)} = \frac{\xi^2}{\xi^2 + \varphi} \quad (8)$$

$$t_- = \frac{\sigma_-}{\sigma} = \frac{eN x_2 \mu_2}{eN(x_1 \mu_1 + x_2 \mu_2)} = \frac{\varphi}{\xi^2 + \varphi}.$$

If we substitute ξ_{\min} it turns out that $t_+ = t_- = .5$ (in that case). We may, therefore, call the conductivity region where $\xi \gg \xi_{\min}$ the region of cation conductivity, where $\xi \ll \xi_{\min}$ the region of anion conductivity.

DISCUSSION OF CONDUCTIVITY OF NaCl DOPED SIMULTANEOUSLY WITH DIVALENT CATIONS AND ANIONS

To get a better understanding of the consequences of the building-in of both kind of admixtures the numerical values of σ/σ_0 and σ resp. were calculated, by varying the parameters of Eq. (4): x_0 was taken according to Btzel and Maurer [14], for the cation association energy the value .34 eV given by Lidiard [12] pg. 310 for cadmium. Some evidence exists that anion complexes might be formed (Miennel [15]). But based on this single evidence hardly a representative value for the association energy can be chosen. The influence of the value of H_2 is discussed, therefore, in general features only. The value of φ was calculated from selfdiffusion data of sodium and chlorine [16]*.

* From the Nernst-Einstein relation it follows that

$$\alpha_+/D_+ = \sigma_+/D_+ = e/kT$$

and in consequence

$$D_+/D_- = \sigma_+/\sigma_- = \mu_1/\mu_2 = \varphi$$

as long as intrinsic values are used, and $x_1 = x_2$.

In Fig. 2a the influence of φ for $H_2 \geq 0$ on σ/σ_0 is demonstrated for fixed values of the other parameters. In the cation conductivity region the influence of φ is of little importance, because $\varphi \ll .3$. The minimum of σ/σ_0

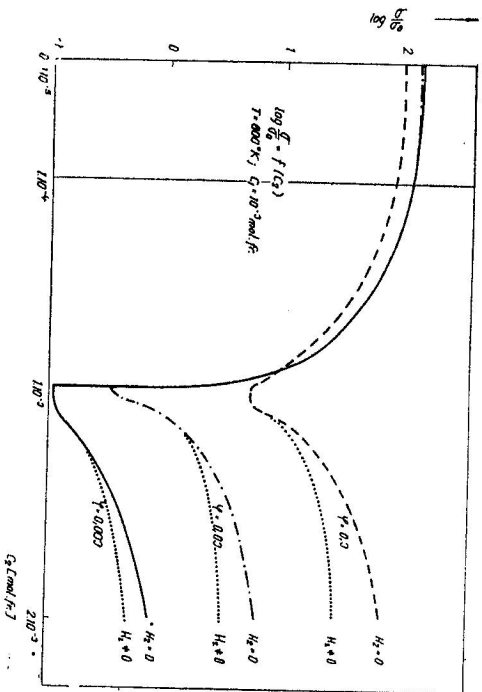


Fig. 2a. The σ/σ_0 isotherm in dependence on anion concentration for different φ .

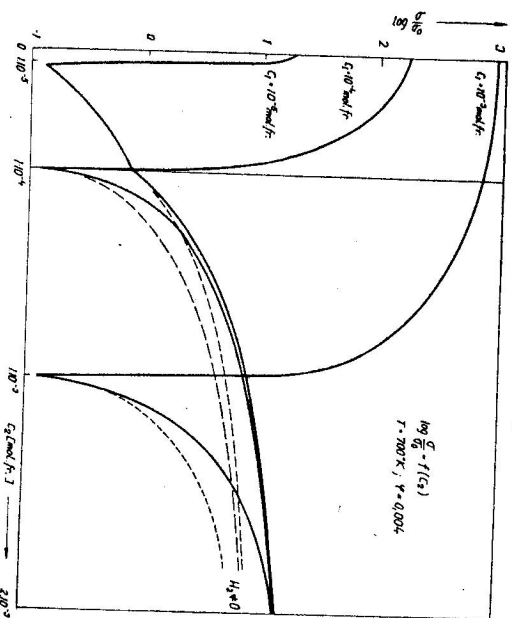


Fig. 2b. The σ/σ_0 isotherm in dependence on anion concentration for different cation concentration.

and the anion region are very sensitive to φ . For high values of c_2 we find σ/σ_0 to be proportional to φ , if $\varphi < 1$. For $H_2 = 0$

$$\frac{\sigma}{\sigma_0} = \frac{\varphi \cdot c_2}{1 + \varphi \cdot 2c_2} \quad (9)$$

But if $H_2 \neq 0$, σ/σ_0 will not be proportional to c_2 .

The influence of c_1 is demonstrated in Fig. 2b. As seen, the overall character of the isotherm is not changed, only the conductivity decrease depends, naturally, on c_1 and the value of c_2 at which the minimum is reached. The influence of the temperature corresponding to the isotherm is seen in Fig. 2c. At lower temperatures the conductivity decrease in the cation region and the increase due to anion conductivity becomes more marked and the minimum becomes more sharp.

The influence of $H_2 \neq 0$ might be easily estimated; it makes itself felt at higher c_2 in the anion conductivity region, where the value of σ/σ_0 is gradually decreasing compared with the case of $H_2 = 0$.

Because conductivity measurements are realized in general by measuring the conductivity of given samples in dependence on temperature, in Fig. 3 the $\log \sigma$ vs. $1/T$ for $c_1 = \text{const.}$ and for several different values of c_2 is given.

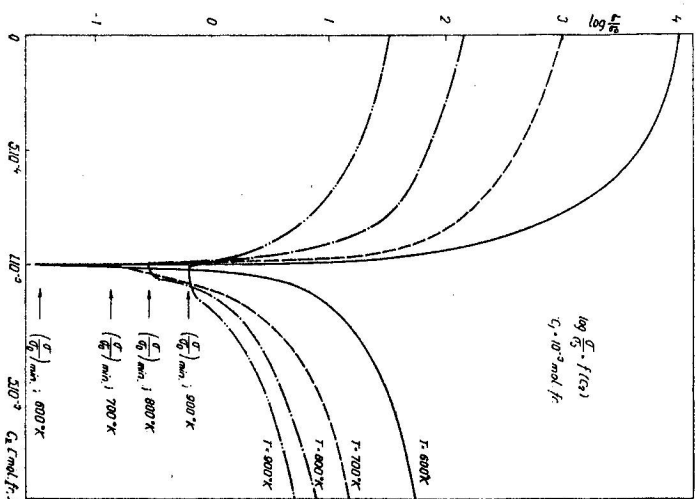


Fig. 2c. The σ/σ_0 isotherm in dependence on anion concentration at different temperature.

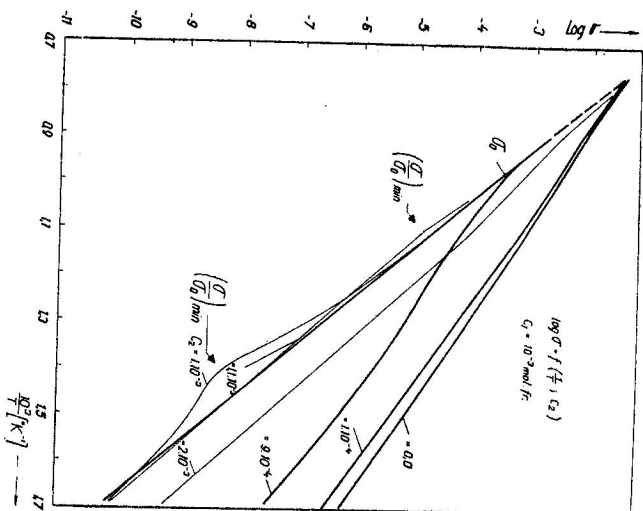


Fig. 3. The $\log \sigma$ vs. $1/T$ curves for different anion content.

As seen the slope of the $\log \sigma$ vs. $1/T$ is increasing with an increasing c_2 . At the same time the first knee shifts against lower temperatures. This change depends on the ratio of $\frac{c_1}{1 + H_1\xi} : \frac{c_2}{1 + H_2\xi}$; if there is a considerable difference $c_1 - c_2$, the change is small, but as soon as c_2 approaches c_1 an abrupt change takes place. Simultaneously the conductivity drops markedly under its intrinsic value. For $c_1 < c_2$ the knee between intrinsic conductivity and admixture conductivity shifts gradually towards higher temperatures and the slope of $\log \sigma$ vs. $1/T$ slowly stops to change. The change in the slope is caused by the change of $1 + H_1\xi$ and $1 + H_2\xi$. Only if $H_1 = H_2 = 0$, no change should occur.

THE INFLUENCE OF AN EVENTUAL QUASI-CHEMICAL REACTION BETWEEN ANIONS AND CATIONS ON THE CONDUCTIVITY

In consequence of the opposite double charge and of the chemical affinity of the anion and cation admixtures and because at least the cation complexes diffuse comparatively quickly, the formation of admixture pairs cannot be

excluded. The formation of such admixture pairs should be described by the quasi-chemical reaction



with an equilibrium given by the mass action law

$$\frac{c_{12}}{(c_1 - c_{12}) p_1 (c_2 - c_{12})} = K'(T). \quad (10)$$

c_{12} denotes the concentration of admixture pairs, $K'(T)$ the respective mass action constant. Because of the assumption that the reaction is realized via cation complex diffusion, the concentration of cations, which did not react with anions ($c_1 - c_{12}$) is multiplied by the degree of association p_1 . In consequence of the formation of neutral molecules in (2a, b) and (3) ($c_1 - c_{12}$), ($1 - p_1$) and ($c_2 - c_{12}$) ($1 - p_2$) should be put for the concentration of dissociated impurities. In consequence in (4) $c_1 - c_{12}$ and $c_2 - c_{12}$ occur instead of c_1 and c_2 . For a constant value of c_{12} the conductivity would correspond simply to a lower value of c_1 and c_2 than indicated by the admixture content of the crystal. Even if c_2 should exceed c_1 , the above features will remain, even if all the cations reacted.

COMPARISON WITH EXPERIMENTAL MATERIAL

From the dependence of conductivity on c_2 as predicted, considerable difficulties may be expected in experiments trying to prove the considered mechanism of conductivity. The conductivity decrease is limited to a very narrow concentration range and it looks very difficult actually to find the minimum. Neither will it always be simple to prove the increase of the conductivity after the minimum has been reached, because of the low solubility of the anion admixtures etc.

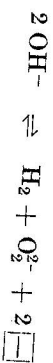
Analysing the up to date published experimental data we shall start with the results published by Rolfe. As it follows from Figs. 5 and 6 [7] the conductivity of KBr is monotonously increased both by CaCl_2 and K_2CO_3 respectively. This behaviour should be expected only in case, when the intrinsic conductivity corresponds to the minimum conductivity of the pure material. In that case $\xi = \xi_{\text{min}} = 1$, $\varphi = 1$ and according to (8) $t_+ = t_- = .5$ should hold. This is just the value of the transport numbers and of φ as established by Jost and Schweitzer [17] for KBr at 600 °C. But even if the true value of φ is .6 at 600 °C as reported by Rolfe [7], our conclusion must hold approximately at least because the value of $(\sigma/\sigma_0)_{\text{min}} = 2 \cdot \sqrt{6/(1 + .6)} = .965$ is hardly to be observed. The high value of φ explains (cf. Fig. 2a) why an increase of σ in the anion conductivity region is observable.

With NaCl Redfern and Pratt, Kessler and Mariani (NaCl: Na₂CO₃), Pashkovskij et al. (NaCl: Na₂CO₃) and with KCl Gruzensky and Scott observed a conductivity decrease with increasing ϵ_2 and most completely and clearly the charts of Kessler and Mariani show a change in the slope of the log σ vs. $1/T$ and a shift of the first knee is seen in accord with Eq. (4). That even NaCl crystals pulled from p. a. material contain some 10⁻³ mol % of cation impurities may be verified from data given by papers [9] and [10] and was confirmed directly for the measured crystals in case of paper [2]: in case of the crystals used by Gruzensky and Scott this fact is borne out by the observed reaction.

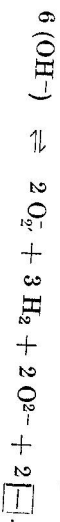
As far as an isotherm-minimum is concerned it was observed only in NaCl doped with Na₂CO₃, which is considerably soluble. It was observed both by Pashkovskij et al. and by Kessler and Mariani. If the low value of φ for NaCl is considered, nothing else would be expected. That CO₂⁻ is built-in into the crystal by Na₂CO₃ doping was ascertained by Kessler and Mariani by pulling the crystal in an inert gas atmosphere.

In spite of the far reaching agreement between theory and experimental results, the latter are still not suitable for a quantitative analysis, with the exception of Rolfe's data.

It should be noted that also NaCl: NaOH (cf. Fig. 1 and 1a [2]) exhibit a behaviour expected according to Eq. (4). As shown in [2] and [5] there does not occur any change of mobility in NaCl: NaOH, neither a reaction between anion and cation admixtures. The authors came to conclude, therefore, that an excess negative charge is formed by the building-in of NaOH*. The fact that the concentration of excess charge, which could explain the change in conductivity is only a small fraction of the anion content of the crystals rather support the theory. This would lead to the assumption that the excess charge is formed by some byproduct of the OH⁻, say OH⁻ in interstitial position or by the formation of O₂²⁻. It should be noted in this connection that the known formation of H₂ in interstitial position could arise e. g. from a reaction like



or (see Voszka et al. [19], who found absorption bands in NaCl: NaOH, which they attributed with reference to Kerkhoff [20] to O₂²⁻)



* If this were true the difference in conductivity of KCl: KOH — Pashkovskij et al. observed an increase, Fritz et al. a decrease — could be explained by differences in purity of the used crystals.

SUMMARY

In this paper the simple association theory of conductivity was generalized and discussed for the case of simultaneously built-in divalent cation and anion admixtures. A comparison of these results with the up to date published experimental material showed a far reaching accordance between theory and experimental data, but with the exception of [7] a quantitative analysis could not be made. The results show also under which conditions proper experiments could be performed.

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