Diffusion in Cubic Sulphates

II. Li^+ and Ag^+ in b.c.c. $(Li,Ag)_2SO_4$

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The diffusion coefficients of silver and lithium in b.c.c. $(Li,Ag)_2SO_4$ have been measured between 470 and 550 °C. D_{Li} and D_{Ag} are equal within the experimental errors. The value of the Nernst-Einstein correlation factor indicates a cooperative motion of ions in the salt.

Nearly equimolar $(Li,Ag)_2SO_4$ forms a high temperature modification with b.c.c. structure. B.c.c. high temperature modifications are also known in e. g. pure AgI and nearly equimolar $(Li,Na)_2SO_4$. For $(Li,Ag)_2SO_4$ and $(Li,Na)_2SO_4$ this leads to unusually complicated phase diagrams [1, 2]. The cubic high temperature phases are characterized by a very high mobility of the cations [3–6]. We have previously reported on conductivity measurements in the $(Li,Ag)_2SO_4$ system [7] and LUNDÉN and OLSSON [8] have studied thermal diffusion in the salt. Since it might be possible to get further information about the transport mechanism in the salt by comparing the diffusivity and the electrical conductivity, we have now measured the diffusion coefficients of silver and lithium in $(LiAg)_2SO_4$.

Since also the transport numbers for the two ions are equal, it is probable that we have a random distribution of the lithium and the silver ions in

Ion	t °C	$D \cdot 10^5$ cm²/s	time min
Li	471	0.523	431
	483	0.454	347
	512	0.771	400
	540	0.906	406
	542	0.977	340
Ag	472	0.425	431
	480	0.528	307
	503	0.687	349
	520	0.738	447
	549	0.962	354

Table 1. The diffusion coefficients of Li^+ and Ag^+ in cubic eutectic $(Li,Ag)_2SO_4$.

The experimental technique has been described previously [9]. The diffusion coefficient for lithium was determined by means of mass spectrometry, while that of silver was obtained by radioactive tracer technique.

The results are given in Table 1 and also in Fig. 1.

The obtained diffusion coefficients can be described by the relations

$$D_{Li} = 0.01611 \exp(-12030/RT), \quad s = 0.058 \cdot 10^{-5},$$
$$D_{Ag} = 0.01600 \exp(-12070/RT), \quad s = 0.036 \cdot 10^{-5},$$

where D is the diffusion coefficient in cm²/s, R the gas constant, T the temperature in °K and s the standard deviation of D.

The two diffusion coefficients are identical within the experimental errors.

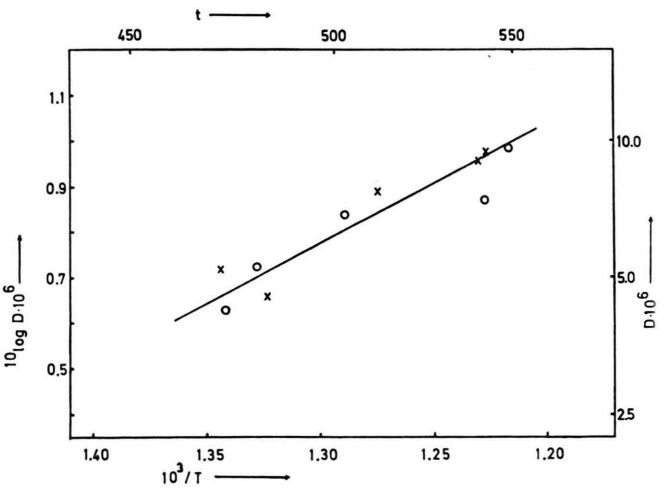

Fig. 1. The diffusion coefficients of lithium and silver in b.c.c. $(Li,Ag)_2SO_4$. ○: Ag^+, × Li^+.

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the salt [1, 7]. A formation of $Ag^+ - Ag^+$ pairs proposed by ØYE [1] should probably lead to a smaller diffusion coefficient for the silver ion than for the lithium ion.

There is a considerable difference in the Arrhenius activation energies for diffusion and electrical conduction in $(Li,Ag)_2SO_4$ (Table 2), but this is the case also for Li_2SO_4 and AgI. Q_D is, however, greater than Q_{cond} in $(Li,Ag)_2SO_4$ and AgI, but smaller than Q_{cond} in Li_2SO_4. We have not found any explanation to this behaviour, but it indicates

Salt	Q_D cal / mole, degr.	Q_{cond} cal / mole, degr.	Ref.
$(Li, Ag)_2SO_4$ (b.c.c.)	12030	7100	7
AgI (b.c.c.)	2230	1180	4, 11
Li_2SO_4 (f.c.c.)	7850	9600	7, 10

Table 2. A comparison between the activation energies for diffusion and electrical conduction.

that the transport mechanism in the f.c.c. and b.c.c. lattices are different and also very complicated.

On the other hand it is possible to compare the measured diffusion coefficient (D_m) with the diffusion coefficient (D_c) calculated from the Nernst-Einstein relation

$$D_c = t^+ \frac{\Lambda}{F^2} \frac{RT}{z^+}.$$

t^+ is the transport number of the cation, z^+ its valency and Λ the equivalent conductivity of the salt. We have assumed that the transport number of the anion is negligible, and since the diffusion coefficients of the two cations are equal it is not necessary to consider the two ions separately. We can thus put $t^+ = 1$.

ØYE [1] has from X-ray data calculated the density of b.c.c. $(Li,Ag)_2SO_4$ at 545 °C and at that temperature we get $D_c/D_m = 2.55$. This ratio becomes still higher at lower temperatures.

For a simple vacancy mechanism we should obtain $D_c/D_m = 1.28$, i. e. equal to the Bardeen-Herring correlation factor, but the value 2.55 indicates a transport mechanism, where several cations cooperate. In e. g. AgI [4, 10] and AgBr [11, 12], D_c/D_m also is greater than two, while the quotient is smaller than one for melts.

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