DIFFUSION OF LITHIUM IONS IN PURE AND DOPED fcc LITHIUM SULFATE

A. Bengtzelius, A. Kvist, A. Lundén

DIFFUSION OF LITHIUM IONS IN PURE AND DOPED fcc LITHIUM SULFATE

A. BENGTZELIUS, A. KVIST and A. LUNDÉN

Department of Physics, Chalmers Institute of Technology,
S-402 20 Gothenburg 5, Sweden

Résumé. — L'influence de la concentration sur la diffusion des ions lithium a été étudiée à 620 °C dans Li_2SO_4 cfc dopé par $MgSO_4$ (jusqu'à 60 % en fraction molaire) ou par LiCl (jusqu'à 13 %). Le coefficient de diffusion D_{Li} diminue lorsqu'on ajoute $MgSO_4$, ce qui est logique si les ions lithium occupent des sites octaédriques, tandis que les cations en positions tétraédriques doivent être considérés comme des interstitiels. A partir de la croissance de D_{Li} avec l'addition de LiCl, l'énergie libre de transfert du Li d'une position octaédrique à une position interstitielle est estimée à 0,37 eV. Des calculs préliminaires sur ordinateur des potentiels ioniques tendent à confirmer ces résultats expérimentaux.

A partir de mesures antérieures de l'effet isotopique, on conclut que le facteur ΔK est voisin de l'unité pour la migration de Li ou Na dans Li_2SO_4, cfc, ce qui signifie que les cations ne partagent pas beaucoup d'énergie avec le réseau des anions lors de leur mouvement. En comparant les données d'autodiffusion et de conductivité, il est conclu à la présence d'une certaine contribution « ring mechanism » s'ajoutant au mécanisme lacunaire pour la migration des ions lithium.

Abstract. — The concentration dependence of the diffusion of lithium ions has been studied at 620 °C in fcc Li_2SO_4 doped with $MgSO_4$ (up to 60 mole %) or with LiCl (up to 18 mole %). The diffusion coefficient D_{Li} decreases when $MgSO_4$ is added, which should be expected if the lithium ions occupy octahedral lattice positions, while cations in tetrahedral positions are to be considered as interstitials. From the increase of D_{Li} when LiCl is added, the Gibbs free energy required to take a Li ion from an octahedral to an interstitial position is estimated to be 0.37 eV. Preliminary computer calculations of ion potentials tend to support these experimental results.

From some previous experiments on isotope effects it is concluded that the so called ΔK-factor is close to unity for the migration of Li or Na ions in fcc Li_2SO_4, which means that diffusing cations do not share much energy with the anion lattice. From a comparison between self-diffusion and conductivity data it is concluded that there is a certain contribution from ring mechanisms in addition to the dominating vacancy mechanism for the migration of Li ions.

1. **Introduction.** — The high-temperature modification of lithium sulfate, stable in the temperature range 572-860 °C, is characterized by a high cation mobility. The sulfate ions are arranged in a cubic (fcc) or pseudocubic lattice [1], in which octahedral and tetrahedral positions are available for the cations. A number of transport studies have been performed in pure Li_2SO_4 as well as in the systems where this salt is one of the constituents. Thus diffusion studies in fcc Li_2SO_4 involve mono- [2]-[4], di- [5] and tri-valent cations [6] as well as some anions [7], and the diffusion coefficients are found to depend on the charge as well as the radius of the diffusing ion. The fairly rapid migration of also rather large anions and cations through the lattice is a consequence of the coupled rotation or strong rotational oscillation that the sulfate ions are performing [1], and which we have compared with a system of cog-wheels [7]. For a model of this type one might question whether it still is reason to talk of distinct jumps [7], while on the other hand our study of the isotope effect of thermomigration supports a simple hole model for Li ion transport in fcc Li_2SO_4, in contrast to the

more collective motion in a liquid [8]. However, whatever model that is preferred for the cation transport, there exists different types of cation positions, and the question is which of these that are preferently occupied by the cations, and which that are vacant most of the time. It should be remembered that for geometrical reasons a cation cannot jump directly between two positions of the same type, and that thus either the octahedral or the tetrahedral positions should serve as intermediate sites for a migrating cation. In order to get information on site preferences, we decided to study the diffusion of Li ions in lattices where the number of vacant cation positions is varied by doping with either a divalent cation (Mg) or a monovalent anion (Cl). In addition some computer calculations are made on a simplified model in order to estimate the energetically most favourable positions.

2. **Experimental.** — There is a considerable solubility of $MgSO_4$ as well as of LiCl in fcc Li_2SO_4 : the phase diagrams of these binary systems have been studied recently in this laboratory [9], [10]. By using

the technique described previously [3] a thin layer of lithium sulfate enriched with $^6Li_2SO_4$ (from Oak Ridge National Laboratory) was deposited on top of an about 70 mm high column of salt of the described composition. After an annealing time of about 4 h at 620 °C, the column was cooled rapidly, and samples taken from the column were analysed with a mass spectrometer in order to determine the isotope abundance ratio $^7Li/^6Li$ as a function of the position. (A more detailed account for experimental details as well as a discussion of possible sources of error is given elsewhere [11].) The calculated diffusion coefficients are listed in tables I and II, and the concentration dependences are shown in figures 1 and 2.

TABLE I

Diffusion of Li^+ *ions in* $(Li_2, Mg)SO_4$ *at 620 °C*

x mole % $MgSO_4$	$D \times 10^5$ cm^2/s	Time min
0	1.90	244
10	1.57	238
20	1.50	240
35	1.23	233
40	1.10	235
50	0.72	960
60	0.60	200

TABLE II

Diffusion of Li^+ *ions at 620 °C in fcc* Li_2SO_4 *doped with LiCl*

y mole % $LiCl$	$D \times 10^5$ cm^2/s	Time min
0	1.90	244
4.9	2.17	260
9.2	2.73	253
14.0	3.32	240
18.2	3.61	248

3. **Computer calculations.** — Flygare and Huggins [12] have recently presented calculations on the transport of ions through crystallographic tunnels in solid electrolytes. We decided to test for a simple model whether tetrahedral or octahedral cation positions are energetically most favourable. We consider the sulfate ions as spheres forming an fcc lattice. The interaction between an arbitrary cation M^{z+} (either Li^+ or an impurity cation) and all other ions is studied. The M^{z+}-SO_4^{2-} interaction is assumed to consist of Coulomb attraction and overlap repulsion, while only Coulomb repulsion is considered for the M^{z+}-Li^+ interaction. The overlap repulsion is expressed by a function of the form $B/(r_i - r)^n$, where r_i is the vector of the SO_4^{2-} ion, r the vector

of the M^{z+} ion, n an integer parameter and B a constant. When calculating the total energy of the mobile cation M^{z+}, all coulombic contributions are included, but for the overlap repulsion only nearest neighbours are considered. A more detailed account of the chosen method and of the results of the calculations is given elsewhere [11]. The choice of the parameters r_0, i. e. the equilibrium distance for the system M^{z+}-SO_4^{2-}, and n becomes more complicated for a polyatomic anion like SO_4^{2-} than for monoatomic ions, since the cations can easily penetrate into the « valleys » between the interpenetrating oxygen atoms. The combination of a large r_0 and low n corresponds to a « soft » sulfate ion, while a small r_0 and a large n would represent the « hard core » of the sulfate ion. In a discussion of the structure of molten sulfates Zarzycki [13] considers 1.94 Å as the shortest possible Li-S distance, but finds from free volume calculations that the average distance is likely to be somewhere between 2.5 and 3.5 Å, i. e. not so far from the average of 3.3 Å interpreted from the X-ray study of fcc Li_2SO_4 [1]. In their calculations on transport in AgI Flygare and Huggins [12] used a repulsion radius for the iodine ion which is somewhat smaller than the Pauling radius, and we decided to start with a hard core calculation with $r_0 = 2.0$ Å and $n = 9$. In this case consistency was obtained for the assumption that each octahedral position is occupied by two Li-ions (the repulsion between the two Li-ions was neglected in this calculation), but not for the alternative that the Li-ions instead are in tetrahedral positions. The next step was to try to calculate the potential barrier a cation has to overcome in order to get from one octahedral position to another. In the calculations done so far, we continued to use short equilibrium distances (r_0) in combination with normal (or high) values of the repulsion parameter n. In this way good agreement was obtained [11] between computed and experimental activation energies for diffusion of mono- and divalent cations in fcc Li_2SO_4. It remains, however, to make computations also for other values of r_0, before one can judge the merits of the chosen model. A further refinement suggested by Krogh-Moe [14] would be to displace the sulfate ion slightly from the fixed position that it has in the present computer model.

4. **Interpretation of isotope effects.** — Information on the transport mechanism can be obtained from isotope effect studies. Two types of isotope effects have been studied previously in fcc Li_2SO_4, and it is reason to adjust the interpretation slightly. A study of simultaneous diffusion of ^{22}Na and ^{24}Na gave a relative difference in diffusion coefficients of $\Delta D/D = 2.8 \pm 0.4$ % [15] and from a comparison of the electrical conductivity of $^6Li_2SO_4$ and $^7Li_2SO_4$ Schroeder and Kvist [16] obtained

$$\Delta\kappa/\kappa = 4.73 \pm 0.40 \text{ %}.$$

Neither isotope effect showed any significant temperature dependence. From these results it follows [17], that

$$f \Delta K_{Na} = 0.64 \pm 0.09$$

and

$$f \Delta K_{Li} = 0.63 \pm 0.05$$

where f is the correlation factor and ΔK represents the distribution or sharing of kinetic energy between the migrating ion and the rest of the lattice. Although the excellent agreement between the diffusion and the conductivity experiment might be fortuitous, it supports the assumption that the transport mechanism is the same for Li^+ and Na^+ ions in fcc Li_2SO_4. Since an octahedral position is surrounded by 8 tetrahedral positions while a tetrahedral position has 4 neighbouring octahedral ones, the correlation factor is not the same for the two types of cation jumps that occur in fcc Li_2SO_4. To our knowledge there are no calculations of the correlation factor for a case like this, but since the average number of neighbouring positions is 6, we expect the correlation factor to be close to that of a simple cubic lattice ($f = 0.6555$), and we then obtain $\Delta K = 0.97$, which does not differ significantly from unity. This means that the diffusing cation does not share much energy with the surrounding anions. Our result is in agreement with a recent calculation for Na^+ diffusion in NaCl, where $\Delta K = 0.998$ was obtained [18].

A comparison for pure Li_2SO_4 between the self-diffusion coefficient [2], D_T, and conductivity data shows that the ratio D_T/D_c (0.91 at 600 °C ; 0.71 at 800 °C) is larger than the assumed correlation factor. This indicates that there is a contribution from a ring mechanism in addition to the vacancy mechanism, with which both Li^+ and Na^+ ions diffuse according to the isotope effect studies discussed above.

5. Interpretation of diffusion in doped Li_2SO_4. —

Let us distinguish for fcc Li_2SO_4 between two types of cation sites, of which most of the α-sites are occupied while most of the β-sites are vacant. Since there is adequate space for two Li-ions in an octahedral position, each such position can be considered as two cation sites, and the number of α- and β-sites thus becomes equal. The energy required to create a vacancy is estimated to be 0.24 eV [11], and thus we might expect that at 600 °C some 80 % of the α- and 20 % of the β-sites are occupied by Li-ions.

The diffusion coefficient is so much less for Mg^{2+} ions than for Li^+ ions ($D_{Mg}/D_{Li} = 0.03$ at 620 °C for nearly pure lithium sulfate [5]) that we can consider the Mg^{2+} ion as immobile when discussing diffusion in doped Li_2SO_4. As shown in figure 1 the diffusion coefficient D_{Li} was found to decrease approximately linearly when the concentration of Mg is increased. An added Mg^{2+} ion replaces two Li^+ ions. If these
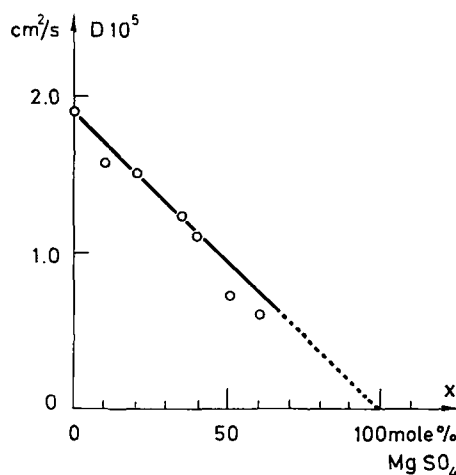

FIG. 1. — Diffusion of Li^+ ions in (Li_2, Mg)SO_4 at 620 °C. The straight line is the concentration dependence to be expected if the Li^+ ions are in octahedral positions, cf. eq. (4).

were occupying tetrahedral positions, the number of vacant tetrahedral positions would increase when Mg^{2+} is added, and we should expect an increase in D_{Li}, but if, on the other hand two Li^+ ions in an octahedral position are replaced by a Mg^{2+}, there will be no change in the number of vacant sites, and due to the increased blocking of tetrahedral sites (see below), D_{Li} should decrease when the mole fraction of $MgSO_4(x)$ is increased. Thus we arrive at the conclusion that the α-sites correspond to octahedral positions, and the tetrahedral positions to interstitial ones, some of which are occupied by activated cations. The system can be treated in analogy with a crystal with Frenkel defects.

Consider a system where we per unit volume have N lattice sites, ($\frac{1}{2} N$ octahedral positions), n_v vacant lattice sites, N_{Li} lithium ions and N_i interstitial positions (= the number of tetrahedral positions times an availability factor ; see below). The mole fraction of $MgSO_4$ is x. Consider migration by a vacancy mechanism for which

G_m = Gibbs free energy of activation [19] ; free energy barrier that opposes the migration [20] ;

G_f = energy required to take a Li ion from an octahedral to an interstitial position (2 G_f required to take an Mg ion to an interstitial position ; the Li^+ and Mg^{2+} ions have approximately the same radius) :

v = vibration frequency (of an ion in the potential minimum) :

a = the jump distance.

We have (a more detailed discussion is given elsewhere [11])

$$n_v = (N_{Li} N_i)^{1/2} \exp(- \tfrac{1}{2} G_f/kT) \tag{1}$$

where $N_{Li} = (1 - x) N$.

The availability of an interstitial position depends on the concentration of Mg^{2+} ions. If immobile

Mg ions surround all tetrahedral positions ($x = 1$), none of these would be available, and $N_i(1) = 0$, while if $x = 0$, we have $N_i(0) = N$. Let us assume that N_i is a linear function of x

$$N_i = (1 - x) N .\qquad(2)$$

The diffusion coefficient for Li ions in $(Li_2, Mg)SO_4$ becomes

$$D = \tfrac{1}{6} fa^2\, v(1 - x) \exp(- [\tfrac{1}{2}\, G_f + G_m]/kT)\qquad(3)$$

or

$$D = (1 - x)\, D_0 \exp(- Q/kT)\qquad(4)$$

where

$$D_0 = \tfrac{1}{6} fa^2\, v \exp([\tfrac{1}{2}\, S_f + S_m]/kT)\qquad(5)$$

and

$$Q = \tfrac{1}{2} H_f + H_m\qquad(6)$$

(S denotes entropy and H enthalpy terms).

D_{Li} increases when LiCl is added to Li_2SO_4, see figure 2, because a vacancy is introduced in the cation substructure, when an SO_4^{2-} is replaced by a Cl^- ion.
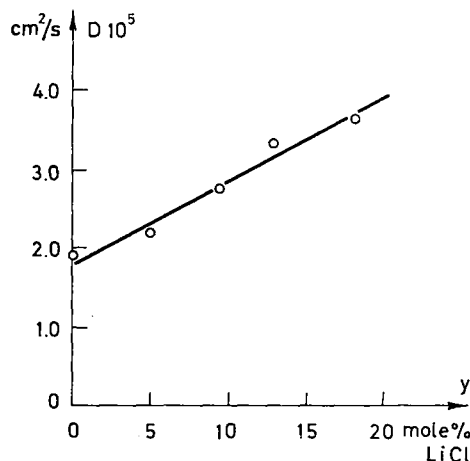

FIG. 2. — Diffusion of Li^+ ions at 620 °C in fcc Li_2SO_4 doped with LiCl. The straight line corresponds to eq. (9).

Thus

$$n_v = (N_{Li}\, N_i)^{1/2} \exp(- \tfrac{1}{2}\, G_f/kT) + N_{Cl} =$$

$$= [N(1 - \tfrac{1}{2}y)\, N_i]^{1/2} \exp(- \tfrac{1}{2} G_f/kT) + \tfrac{1}{2} Ny\qquad(7)$$

where N_{Cl} is the number of Cl ions per unit volume, and y is the mole fraction of LiCl. With the approximation $[N(1 - \tfrac{1}{2}\, y)\, N_i]^{1/2} \simeq N$, we obtain the diffusion coefficient for Li ions in $Li_2(SO_4, Cl_2)$

$$D = \tfrac{1}{6}\, fa^2\, v \exp(- G_m/kT)[\exp(- \tfrac{1}{2} G_f/kT) + \tfrac{1}{2} y]\qquad(8)$$

or

$$D = A + By .\qquad(9)$$

Thus

$$G_f = 2kT\, \ln(2\, B/A) .\qquad(10)$$

From the experimental data we obtain $A = 1.813 \times 10^{-5}\ cm^2/s$, $B = 10.28 \times 10^{-5}\ cm^2/s$ and $G_f = 0.37$ eV.

The activation energy for cation self-diffusion in pure Li_2SO_4 is $Q = 0.34$ eV [2], and if we approximate $H_f = G_f$, it follows from eq. (6) that $H_m = 0.15$ eV. This experimental result can be compared with computed values of the potential barrier for migration of Li ions. So far we have made a computation only for the combination $r_0 = 1.91$ Å and $n = 7$, which gave $H_m = 0.24$ eV [11]. The agreement between the two values of H_m is satisfactory, if one considers the approximations involved in the simple model used for the computations and in the interpretation of the experiments. E. g. when calculating G_f by means of eq. (10), we have assumed that the observed increase in D_{Li} with increasing y is due only to an increase in the number of vacant cation sites. We know, however, that D_{Cl} increases too when LiCl is added [7], and there is reason to believe that deformation of the anion lattice and changes of the rotational properties of the sulfate ions has some influence also on D_{Li}. If one should assume that, say, 20 % of the coefficient B in eq. (9) had other causes than the increase in the number of vacancies, this would change G_f to 0.34 eV and H_m to 0.18 eV. When deriving eq. (8) we have assumed that G_m and G_f are independent of the composition of the mixture. This has not been checked experimentally for diffusion, but it is known that the activation energy of conductivity is approximately the same in the whole concentration range [7].

6. General conclusions. — If, in addition to the diffusion studies and computer calculations (which so far are to be regarded as preliminary), one also considers investigations of conductivity, electromigration and thermomigration in Li_2SO_4-rich fcc phases, one finds that difficult problems remain to be solved concerning the migration of large cations, such as potassium [21], but it is also evident that all the results seem to be consistent with a model where the lithium ions normally occupy octahedral positions, and where the transport of at least lithium and sodium ions predominantly takes place by a vacancy mechanism with a certain contribution from some kind of ring mechanism.

References

[1] FØRLAND, T. and KROGH-MOE, J., *Acta Chem. Scand.* **11** (1957) 565.

[2] KVIST, A. and TROLLE, U., *Z. Naturforsch.* **22a** (1967) 213.

[3] KVIST, A. and BENGTZELIUS, A., *Z. Naturforsch.* **23a** (1968) 679.

[4] INMAN, D. and JOHNSON, M., *J. Appl. Electrochem.* **2** (1972) 347.

[5] KVIST, A., BENGTZELIUS, A. and TROLLE, U., *Z. Naturforsch.* **23a** (1968) 2042.

[6] BENGTZELIUS, A., JOSEFSON, A.-M., KVIST, A. and SCHROEDER, K., *Z. Naturforsch.* **25a** (1970) 1921.

[7] KVIST, A. and BENGTZELIUS, A., *Fast Ion Transport in Solids*, ed. van Gool, W. (North-Holland Publ. Co., Amsterdam) 1973, p. 193.

[8] LUNDÉN, A., *Atomic Transport in Solids and Liquids*, ed. Lodding, A. and Lagerwall, T. (Verl. Z. Naturforsch., Tübingen) 1971, p. 302.

[9] TÄRNEBERG, R., LJUNGMARK, H., KVIST, A. and BENGTZELIUS, A., unpublished.

[10] LJUNGMARK, H. and KVIST, A., unpublished.

[11] BENGTZELIUS, A., Thesis, University of Gothenburg 1973.

[12] FLYGARE, W. H. and HUGGINS, R. A., *J. Phys. Chem. Solids* **34** (1973) 1199.

[13] ZARZYCKI, J., *Disc. Faraday Soc.* **32** (1961) 38.

[14] KROGH-MOE, J., Priv. Com.

[15] BENGTZELIUS, A. and KVIST, A., *Z. Naturforsch.* **24a** (1969) 468.

[16] SCHROEDER, K. and KVIST, A., *Z. Naturforsch.* **25a** (1970) 1365.

[17] LE CLAIRE, A. D., *Phil. Mag.* **14** (1966) 1271.

[18] BROWN, R. C., WORSTER, J., MARCH, N. H., PERRIN, R. C. and BULLOUGH, R., *Phil. Mag.* **23** (1971) 555.

[19] LIDIARD, A. B., *Handbuch der Physik* **20** 246 (Springer-Verlag, Berlin) 1957.

[20] BÉNIÈRE, F., *Physics of Electrolytes*, Vol. 1, p. 203, éd. Hladik, J. (Academic Press, London) 1972.

[21] LUNDÉN, A., FLOBERG, M. and MATTSSON, R., *Z. Naturforsch.*, in the press.