On the Paddle-Wheel Mechanism for Cation Conduction in Lithium Sulphate

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A few high-temperature sulphate phases are both plastic crystals and solid electrolytes, the latter because the hindered rotational motion of the sulphate ions enhances the mobility of the cations. This interpretation has been called the paddle-wheel model, and it is obvious that cation migration becomes a much more complicated process in a plastic ionic crystal than in a crystal with a stiff, time-independent structure. Thus, there are strongly enhanced contributions from conventional migration mechanisms, such as jumping from well-defined lattice sites, but it is evident that there also are contributions which are specific for the paddle-wheel mechanism. By the molecular dynamics study by Ferrario, Klein and McDonald it has become possible to identify separately the contributions from centre-of-mass displacements and rotations of the sulphate group. Information in this direction has also been obtained recently by Karlsson and McGreevy in a neutron powder diffraction study where the reverse Monte Carlo method is used for modelling the data. The latter authors have modified the terminology slightly, which causes confusion regarding the meaning of the term "paddle-wheel mechanism". The "paddle-wheel" enhances not only bulk migration but also migration along interfaces and surfaces. The mobility can also be increased for monovalent anions present. Some examples are given of other types of mobility enhancements which also are due to libration or rotation of polyatomic anions.

1. Introduction

A group of four high-temperature phases, Li_2SO_4, $LiNaSO_4$, $LiAgSO_4$, and $Li_4Zn(SO_4)_3$, are both plastic crystals and solid electrolytes. This means that ion transport becomes more complicated than in other inorganic ionic compounds. The concept "paddle-wheel model" (or originally "cogwheel model") was introduced as a short name for a very complicated situation, where the relative importance of the different processes is not the same for e.g. Li^+, Na^+, and K^+ ions. However, in a recent paper [1] the term "paddle-wheel mechanism" was limited to cover only one of the contributing processes, which can cause some confusion. The purpose of this paper is to identify three types of contributions to ion migration between two sites. First we have the attempts by a cation to make a jump. As is wellknown, the probability for a successful jump is limited by the height of the potential barriers. In the paddle-wheel case, the shapes of saddlepoints and potential barriers will vary all the time, due, inter alia, to centre-of-mass displacements of the sulphate groups. This contribution to the overall transport is called "percolation" by some authors (1). Then there is the possibility that the cations are more or less strongly associated with the oxygen atoms of the sulphate ions, and that they thus are following along with the rotation.

A large number of salts with polyatomic anions have been studied at least to some extent in the last decades, and it has been proposed occasionally that libration or rotation of anions enhances cation migration. Some authors have spoken of "cogwheel", "paddle-wheel" or "swingdoor" mechanisms. Similarities and differences between some groups of salts will be discussed in Sect. 10 and 11.

2. Growth of Knowledge

The phases of the four salts mentioned above are very similar in their properties, while there are distinct differences not only relative to phases with a "normal", i.e. low, ionic conductivity but also with regard to other types of solid electrolyte phases, such as bcc AgI. Førland and Krogh-Moe studied the structure of the high-temperature phase of Li_2SO_4 [2], which was found to be fcc. However, they remarked that strong rotational orientations must be expected for the sulphate groups, and "that the lithium ions most probably can exchange between tetrahedral and octahedral lattice positions". Førland and Krogh-Moe measured

the electrical conductivity in order to verify this latter assumption, and they found that it is of the same order in the high temperature phase as in the fused state [3]. This is the case also for the bcc phases of LiNaSO$_4$ and LiAgSO$_4$ which were discovered by Førland and Krogh-Moe [3], and by Øye [4, 5], respectively, as well as for the non-cubic phase of Li$_4$Zn(SO$_4$)$_3$ [6, 7]. Øye presented alternative models for the spatial orientation of the sulphate ions in fcc Li$_2$SO$_4$ [4].

It was known at that time that a light isotope is more mobile than a heavy one in bcc AgI [8, 9] as well as in molten salts [10], and we performed electromigration experiments which showed that the isotope effect for lithium ions was the same in solid fcc Li$_2$SO$_4$ [11] as in molten lithium halides [10, 12], while it was somewhat smaller in molten LiNO$_3$ [13]. The isotope effects measured in the quoted early studies fit well with a very simple interpretation where one distinguishes between spontaneous and induced jumps, where only the spontaneous ones depend on the mass of the migrating ion [14].

We performed a series of diffusion experiments in 1966–1973; for references see [15]. The interpretation has been updated recently under consideration of the latest information from other types of studies [16]. It had gradually become evident that neither the diffusion coefficients nor the activation energies showed the type of correlation with the ionic radii, which one would expect from conventional diffusion models. Thus, cation migration could not be due only to hops between well-defined lattice positions, and we concluded that the hindered rotational motion of the sulphate ions enhanced the migration of mono- and divalent cations. We called this interpretation the "cogwheel" model [17]; the name was later changed to the "paddle-wheel" model [18].

A study by neutron powder diffraction showed no traces of Li$^+$ ions in the octahedral positions (1/2, 1/2, 1/2) of fcc Li$_2$SO$_4$ [18]. This was also the case for our single-crystal neutron diffraction study, which fitted best to a model where 90% of the Li$^+$ ions are in tetrahedral positions, (1/4, 1/4, 1/4) etc., with the remaining 10% of them located in a spherical shell, which surrounds the sulphate ions [19].

There have been two comprehensive studies of cubic lithium sulphate by molecular dynamics (MD) [20, 21]. The second one considered three compositions, namely pure fcc Li$_2$SO$_4$, a fcc solid solution Li$_{1.75}$Na$_{0.25}$SO$_4$ and equimolar bcc LiNaSO$_4$. It was found that "the cations are almost invariably bonded

to one and often to two oxygen atoms of neighbouring sulphate groups. The latter therefore play an essential role in the cation diffusion mechanism." An advantage with MD is that one can vary the mass and the radius of the considered atoms over very wide ranges. It has in this way been possible to divide the diffusion coefficient in three terms

$$D = D_{latt} + D_{gate} + D_{reor},$$

where D_{latt} corresponds to "the movement of cations through a disordered but static structure", D_{gate} to the temporary opening of a "gate" due to centre-of-mass fluctuations of the sulphate ions, and D_{reor} is the contribution from reorientations of the anions. The relative importance of the three D-terms is not the same for Li$^+$ and Na$^+$, and it depends on the composition of the sample, too. This will be discussed in more detail below, see Section 3.

Karlsson and McGreevy have measured the total structure factors, i.e. both Bragg and diffuse scattering, for Li$_2$SO$_4$ and LiNaSO$_4$ by powder neutron diffraction, and they have used the reverse Monte Carlo (RMC) method for modelling the data [1]. They find that the ionic conduction in the two cubic phases is due to two types of motion "and everything in between", i.e. the change between the two types of motion is gradual.

There has of course been work done on sulphate plastic crystals by others than those mentioned here, but we can, for simplicity, distinguish between three sources of information: studies done by a rather large number of cooperating scientists using quite many experimental techniques [22–26], the MD simulations [20, 21] and the RMC work [1]. The consistency between these three sources of information is, on a whole, better regarding Li$_2$SO$_4$ than for LiNaSO$_4$, and I will concentrate on comparisons concerning the fcc phase between the recent MD simulations [21] and earlier experimental studies.

3. Cation Jumps

As said above, the electromigration experiments showed not only that ^{6}Li migrated faster than ^{7}Li, but also that there was a similarity between fcc Li$_2$SO$_4$ and the molten halides LiCl, LiBr and LiI. Furthermore, there is evidence that the isotope effect of sulphate does not change at the melting point [27]. (In this study molten mixtures of Li$_2$SO$_4$ and K$_2$SO$_4$ were chosen instead of pure molten Li$_2$SO$_4$; some

materials problems were avoided by working at lower temperatures.) An isotope effect has also been detected for the electromigration of Li^+ in solid LiH [28], which has an ionic conductivity of 0.0037 S/cm at 873 K. (There is no discontinuity in the electrical conductivity at the melting point of LiH [28]. LiH is similar to $LiNaSO_4$ and $LiAgSO_4$ in this respect.) As mentioned above, an isotope effect for electromigration was reported already in 1944 for Ag^+ ions in bcc AgI [8, 9]. Furthermore, the electrical conductivity is higher for $^6Li_2SO_4$ than for $^7Li_2SO_4$ in the solid as well as in the melt [29], and thermomigration results in an enrichment of ^6Li on the hot side [30].

The isotope effect has been measured for the diffusion of Na^+ in fcc Li_2SO_4 by using the radioactive tracers ^{22}Na and ^{24}Na in the range 967–1049 K [31]. The difference between $D(^{22}Na)$ and $D(^{24}Na)$ was found to be 2.8%, while the difference between the square roots of the masses is 4.3%. An isotope effect was studied also in the MD simulations for bcc $LiNaSO_4$ at 873 K [21]. Thus $D(^7Na)$ was found to be 2.69×10^{-5} cm^2/s, while $D(^{23}Na)$ was 2.03×10^{-5} cm^2/s, i.e. $D(Na)$ is 33% larger for the "light" isotope than for the natural one. There is reasonable agreement between the simulated isotope effect and the measured one.

$D(Li)$ and $D(Na)$ are nearly equal in both fcc $Li_{1.75}Na_{0.75}SO_4$ and bcc $LiNaSO_4$ according to the MD simulations [21], and there is no significant difference between these two diffusion coefficients according to measurements in Li_2SO_4, $LiNaSO_4$ or $LiAgSO_4$, at least not when the data are considered for temperatures near 823 K [16]. However, MD simulations show that D_{latt} is significantly smaller for Li^+ than for Na^+, while it is the other way round for the sum $(D_{gate} + D_{reor})$ [21]. This is not surprising, since the radius of a Li^+ ion is actually smaller than corresponding to the optimal ion size for cation migration in our cubic sulphate lattices. This is also indicated by the fact that the above-mentioned "artificial" $D(^7Na)$ is 27% larger than $D(^7Li)$; the latter is 2.11×10^{-5} cm^2/s at 873 K [21].

It might be reason to remind of the fact that there are other solid materials where Li^+ ions are less mobile than larger ions, such as Na^+ and Ag^+. The most wellknown case is probably the beta-aluminas. Diffusion of the abundant cation has been measured in several of these materials [32]. E.g. at 625 K, $D(Li)$ is 0.13×10^{-5} cm^2/s in lithium beta-alumina, while $D(Na)$ is 1.1×10^{-5} cm^2/s in sodium beta-alumina.

D_{latt} is simulated by increasing the total mass of each oxygen atom by 1600 amu, which freezes both the translational and rotational degrees of freedom of the ion. D_{latt}/D is 30% for fcc $Li_{1.75}Na_{0.25}SO_4$ (average for Li^+ and Na^+) and 25% for bcc $LiNaSO_4$. However, the freezing means that we no longer are dealing with plastic crystals. As said above, neither Førland and Krogh-Moe [2] nor Øye [4] could find any really satisfactory structure for such a phase. According to the quoted MD simulations, the ion mobilities should still be of the same order of magnitude for the fcc and bcc phases, while one should expect that the ion mobilities are at least an order of magnitude lower in the frozen fcc phase than in the frozen bcc one. The reason is that only 1/3 of the cation lattice sites (tetrahedral and octahedral sites) are vacant in the fcc sulphate structure, while 7/9 of these sites are empty in the bcc structure. It is of interest to compare with two iodides with solid electrolyte phases, namely (the disordered high-temperature phase of) fcc Ag_2HgI_4 and bcc AgI. 1/4 of the cation lattice sites are vacant in the fcc phase, but 5/6 in the bcc phase (when only tetrahedral sites are considered for AgI). For Ag_2HgI_4 we have $D(Ag^+) = 0.09 \times 10^{-5}$ cm^2/s and $D(Hg^{2+}) = 0.0005 \times 10^{-5}$ cm^2/s at 373 K, with the activation energies 0.4 eV and 1.0 eV, respectively [33]. (The data for Ag_2HgI_4 are estimated from a plot.) Extrapolation to 373 K gives $D(Ag^+) = 0.85 \times 10^{-5}$ cm^2/s for bcc AgI; the activation energy is 0.097 eV [34].

4. The Role of the Anions

As said above, our studies of cation diffusion convinced us that the high rate of cation migration could not be due to a conventional hopping mechanism. This suspicion was actually supported by data concerning the temperature dependence of the electrical conductivity. In general, one can expect that the activation energy is low for salts with a high conductivity and vice versa. Let us compare bcc AgI and fcc Li_2SO_4. If we extrapolate the conductivities of both salts to 823 K we obtain 2.69 S/cm^2 for bcc AgI and 1.07 S/cm^2 for fcc Li_2SO_4, while the activation energies, $Q(\sigma T)$, are 0.11 eV and 0.43 eV, respectively [16]. The corresponding figures for bcc $LiNaSO_4$ are 1.25 S/cm^2 and 0.44 eV. The activation energies of the two sulphates are close to the $Q(\sigma T) = 0.36$ eV of (disordered) fcc Ag_2HgI_4 [35]. The conductivity of the

latter phase is 0.0016 S/cm at 328 K; to be compared with an extrapolated conductivity of 0.69 S/cm for bcc AgI at 328 K [36], for which $Q(\sigma T)$ is 0.11 eV. It should be mentioned in passing that there are considerable discrepancies in the literature concerning the conductivity of fcc Ag_2HgI_4, for which it usually is overlooked that small amounts of impurities or minor deviations from stoichiometry frequently are introduced during the preparation of the salt [35]. It is likely that the cation diffusion coefficients quoted in Sect. 3 above are less sensitive for impurities etc. than the conductivity is.

Secco suggested in 1986 [37] that "convincing evidence" could be obtained for or against the paddle-wheel model by studying the conductivity of solid solutions where the sulphate had been partially substituted by tungstate ions. This should lead to a reduced conductivity if the paddle-wheel mechanism is of importance, see also Sect. 5, below. Actually, Kvist had reported already in 1967 that the conductivity was lower for a sample with 2 mole% tungstate than for the pure sulphate [38]. A later study by Dissanayake et al. showed a decreasing conductivity for the sequence of 2.5, 3.0 and 3.5 mole% added tungstate, while the conductivity was higher than for the pure sulphate if 4.0 mole% of sulphate had been added [39]. The latter is because the solid solubility of tungstate had been exceeded, i.e. the sample corresponded to a two-phase region (fcc + liquid). Unfortunately, Secco et al. had chosen to investigate a mixture containing 10 mole% of tungstate, and the dimensions of their sample were not suitable [40], so they reported a tremendous conductivity increase [37], cf. Sect. 5, below.

It has all the time been obvious to us that "the occasional lowering of potential thresholds makes it easier for a vibrating ion to jump to an empty position" [41]. The shape, height and position of potential barriers varies continuously both due to changes of the distances between the oxygen atoms of neighbouring sulphate ions, and to variations in the distances between the centres-of-mass of the sulphate ions. The question of O–O distances was discussed already by Førland and Krogh-Moe in 1957 [2]. Our neutron powder diffraction study showed that the temperature factor was high for the SO_4^{2-} ion [18], which means that there is a considerable displacement of the centre-of-mass of the sulphate ions. While it thus has been obvious all the time that continuous changes in the potential barriers contribute to the enhancement of cation mobility, it was first in our single-crystal experiment that we found direct evidence for rotational transport of the cations [19]. The recent MD and RMC studies have not only confirmed this latter contribution, but it has become possible to estimate the relative importance of different types of contributions.

As said in Sect. 2, our single-crystal neutron diffraction experiment [19] supports a model where the lithium ions are located either in tetrahedral sites or in a sphere surrounding the sulphate ion. Two types of jumps occur in this simple model: from a site to the sphere, and from the sphere to a vacant site. If we apply the simplified model of isotope effects mentioned in Sect. 2 [14], the jumps to the sphere are spontaneous, while the jumps to a vacant site are induced. The latter holds also for jumps triggered by the changes in the potential threshold, i.e. processes labeled as "gating" [21] or "percolation" [1].

5. A Comment on a Controversy

As said in Sect. 4, Secco et al. reported in 1986 that they had shown "convincingly that anion-rotation 'cogwheel' or 'paddle-wheel' mechanism does not contribute to the high mobility of Li^+ in Li_2SO_4-based compounds" [37]. They state that the extremely large conductivity is due to "simple physical sublattice expansion or by vacancies on normal lattice sites in terms of a percolation type mechanism". On a later occasion Secco goes into more detail [42]. He still claims that "free volume in the lattice framework plays a predominant role", but he recognises that "the rotating sulphate ions ... may contribute to the conductivity, ... but (only) indirectly ...". However, already in my first comment on Secco's ideas I had written that "we have always considered the mechanism to be very complicated", and I mentioned that one of the reasons for the high mobility is that "the occasional lowering of potential thresholds makes it easier for a vibrating ion to jump to an empty adjacent position" [41]. In summary, although we have not had any information on their relative importance, we have always expected that there should be contributions of all the types studied recently by MD and RMC. On the other hand, Secco has again and again denied the possibility of D_{reor}. It is likely that many people think that the discrepancy was larger than it actually has been. Indeed, there have been lengthy discussions, for references see [43], but much has dealt with peripheric

issues. Anyhow, it is correct to say that the MD and RMC studies have confirmed our paddle-wheel concept to 100%.

6. The bcc Phases

It is beyond the scope of this paper to make detailed comparisons between the results of different studies. However, one might mention that the highest density of Li^+ ions was found in the tetrahedral sites of fcc Li_2SO_4 according to all types of studies, i.e. our neutron diffraction [18, 19], the MD simulations [21] and the RMC work [1], while it was only in the latter study that traces of Li^+ ions were detected in the octahedral sites. Actually, some Li^+ ions jumped via the octahedral sites according to the RMC, while the Li^+ ions outskirted these sites owing to the single-crystal study [19] and the MD simulation [21]. It is not surprising that there are minor differences of the mentioned types. While our knowledge appears to be good concerning the mean features of fcc Li_2SO_4, the situation is not as good when it comes to the bcc phases. We shall limit the discussion to some comments on bcc $LiNaSO_4$, which has been studied by many techniques, including (conventional) neutron powder diffraction [44], MD [21] and RMC [1]. While the results of our neutron diffraction study fit best to a model where all the Li^+ ions are in tetrahedral sites and all the Na^+ ions in octahedral sites, both cations are distributed over several types of sites according to the RMC and MD studies. Details are given in the publications. Inter alia, according to the RMC, the highest density of Na^+ is found in the octahedral sites [1], while the MD shows a Na^+ distribution with 41% in tetrahedral, 10% in octahedral and 49% in other sites [21]. The mentioned recent studies present much information on preferred directions for conduction pathways, transport mechanisms etc. for Li^+ and Na^+ ions in bcc $LiNaSO_4$. As expected, there are significant differences between the two cations.

Differences have been detected between fcc Li_2SO_4 on one hand and the two bcc phases on the other concerning some properties. This is the case for a recent survey of cation diffusion data, see [16]. Another example is the enthalpy of melting, which is 3.4 kJ/mole for $LiAgSO_4$ [4], while it is 9 kJ/mole for Li_2SO_4 [16]. (The enthalpy of the solid-solid transition is 28.3 kJ/mole for $LiAgSO_4$ [4], and it is 24.8 kJ/mole for Li_2SO_4.) Krogh-Moe included entropy data in a

discussion where he concluded that a group of high-conductivity bcc phases (AgI, CuBr, Ag_2S, Ag_2Se, $LiAgSO_4$ and $LiNaSO_4$) are more "liquid-like" than high-conductivity fcc phases, such as the (disordered) Ag_2HgI_4 mentioned in Section 3 [45]. From this point of view, it is not surprising that Karlsson and McGreevy conclude from their RMC study that the situation is even more complex in $LiNaSO_4$ than in Li_2SO_4, and that the mechanism of cation conduction is not as obvious in the bcc salt as in the fcc salt.

I have given some data for fcc Ag_2HgI_4 and bcc AgI in Section 3. It is interesting to note that the difference between fcc and bcc phases is much smaller for the plastic cubic sulphates than for the iodides. This leads to the conclusion that the enhancement of cation mobility due to the rotational motion of the sulphate ions is definitely larger for the fcc phase than for the bcc ones. Adding to the discussion in the end of the preceding paragraph, one might say that fcc Li_2SO_4 is more "liquid-like" than fcc Ag_2HgI_4.

7. Interface and Surface Migration

It is found for diffusion of monovalent cations in fcc Li_2SO_4 that both the diffusion coefficients and the activation energies decrease when the radius increases [16]. However, the solid solubility decreases too, and an at least qualitative explanation of the mentioned "anomaly" is that bulk diffusion dominates for ions which are quite soluble, while migration of large ions mainly takes place along high-diffusivity paths, interfaces and surfaces. It is evident that the "paddle-wheel" enhances also these latter types of diffusion.

8. Phase Transitions

It was observed by Førland and Krogh-Moe that the relative X-ray intensities of a sample of monoclinic Li_2SO_4 were different before and after the sample had been kept for a while in the fcc phase [2]. This shows that preferred orientation is taking place.

A more drastic effect can be observed with the naked eye if a melt (Li_2SO_4 or $LiNaSO_4$) is solidified and cooled till below the transition to the monoclinic phase, and then is heated and brought back to the cubic phase [46]. If the cooling is done rather slowly, the virgin plastic phase is as transparent as the melt. The salt becomes opaque when the solid-solid transi-

tion sets in, and it remains opaque if the transition is passed during a heating mode. Obviously, the fresh solid salt was neither a single crystal nor amorphous, but, due to the plasticity, non-visible regions of gradual reorientation of crystal axes were obtained instead of grain boundaries. Such regions might serve as high-diffusivity paths in the plastic phase. Once grain boundaries had been created at the transition to the monoclinic phase, they remained when the structure went back to the cubic phase [46].

It might be reason to take up the interpretation of studies of light scattering in this connection. It has been said that bandwidth data for Raman scattering can be taken as evidence against the "paddle-wheel" [42, 47]. It is true that a drastic change of the activation energy for reorientation of the sulphate ions has been reported to occur for lithium sulphate near 725 K [48], i.e. within the reign of the monoclinic phase, and far from any observed structural transition. However, the Raman spectra are also affected by structural phase transitions. It is namely explicitly said [49–52] that fcc Li_2SO_4, bcc $LiNaSO_4$ and bcc $LiAgSO_4$ are plastic phases, and that their Raman spectra show features which do not exist for their room-temperature phases or for hexagonal Na_2SO_4.

9. The Melt

As said in Sect. 2, similarities were found very early between cubic and molten sulphate phases. However, differences were also detected. Thus, while the conductivity at the melting point is nearly the same for the solid and the melt, as reported by Førland and Krogh-Moe [3], the activation energy is significantly lower for the melt. E.g. for pure Li_2SO_4 $Q(\sigma T)$ is of the order of 0.25 eV above the melting point and 0.41 eV in the region below [53]. (The "activation energy" of fcc Li_2SO_4 decreases when the temperature is increased.) The corresponding $Q(\sigma T)$ are 0.30 eV and 0.44 eV, respectively, for $LiNaSO_4$ [36], while they are 0.26 eV and 0.40 eV, respectively for $LiAgSO_4$ [54]. $Q(\sigma T)$ is 0.26 eV for pure molten Na_2SO_4 [36], and 0.20 eV for pure molten Ag_2SO_4 [54]. Another difference between the two states is that our diffusion studies as well as the MD simulations show that the mobilities are nearly the same for Li^+, Na^+, and Ag^+ in the cubic phases, see Sect. 3 above, while there are pronounced differences between their mobilities in the molten state. Since no diffusion studies have been performed

in sulphate melts, we can only base this conclusion on a comparison of the electrical conductivities. Thus at 1173 K we have 4.39 S/cm for Li_2SO_4 [53], 2.88 S/cm for $LiNaSO_4$ [36], 2.79 S/cm for $LiAgSO_4$ [54], 2.31 S/cm for Na_2SO_4 [36] and 2.26 S/cm for Ag_2SO_4 [54]. (The data for $LiNaSO_4$, $LiAgSO_4$ and Ag_2SO_4 are extrapolated.)

It is characteristic for the plastic high-temperature sulphate phases that the enthalpy of melting, ΔH_m, is very small, while the enthalpy of the solid-solid transition, ΔH_t, is large. Thus, $\Delta H_m = 9$ kJ/mole and $\Delta H_t = 24.8$ kJ/mole for Li_2SO_4, while $\Delta H_m = 3.4$ kJ/mole and $\Delta H_t = 28.3$ kJ/mole for $LiAgSO_4$ [4]. The ratio $\Delta H_m/\Delta H_t$ is thus significantly smaller for the plastic solid electrolytes than for other ones, cf. e.g. $\Delta H_m = 5$ kJ/mole and $\Delta H_t = 6.3$ kJ/mole for AgI.

The structure of molten Li_2SO_4 has been studied by X-ray diffraction on several occasions [55], and a neutron diffractogram has been collected at Risø National Laboratory, Denmark [56]. The TAS IV triple-axis spectrometer was used in the mode of a powder diffractometer. Scattering data obtained at 1223 K were compared with the diffuse scattering recorded in our previous studies of fcc Li_2SO_4 [18, 44]. A Fourier transformation by the Zernicke-Prins formula showed good agreement concerning the positions of three maxima and the depressions lying between. Our liquid-data transform was also in good agreement with the analysis of X-ray-data by Ohno and Furukawa [57]. They had concluded that the liquid structure was likely to be closely related to the fcc structure. This is confirmed by our neutron work. Thus, the only differences between the structures of liquid and cubic lithium sulphate are that there is long-range order in the fcc phase and that the sulphate lattice is translationally fixed in the fcc phase [56].

10. Some Other Solid Phases

Much interest has been devoted in recent years to cation conduction in various salts with polyatomic anions. High ionic conductivities have been observed in many cases, and it has been suggested that the conductivity is enhanced due to librational motion or hindered rotation of the anions. The label "paddle-wheel" has occasionally been used. I shall here comment briefly on a few types of salts with three-dimensional AB_4 anions.

It is very common for sulphates that the high-temperature phase is hexagonal. The by far most studied one is Na_2SO_4, but quite many studies have concerned Ag_2SO_4 and K_2SO_4. The conductivity of pure Na_2SO_4 is 0.069 S/cm at 1073 K, and the activation energy ranges between 0.5 and 1.7 eV [58]. The situation is similar for $Ag_2SO_4(I)$ for which the activation energy is 1.2 eV in the range 739–917 K [54]. Partial substitution of Na^+ (or Ag^+) ions by aliovalent ions creates vacancies, and the conductivity is strongly enhanced to begin with. However, there is always a limit beyond which the conductivity either decreases [59, 60] or remains constant [61]. It seems likely that dopant ions and vacancies form clusters which limit the conductivity. An unexpected discovery is that partial substitution of Na^+ by Li^+ causes a large enhancement of the conductivity of $Na_2SO_4(I)$ over the whole solubility range [62], and the cations diffuse very fast [63]. The cause of this mobility enhancement is that the solute Li^+ ions prefer interstitial sites which are smaller than the Na^+ sites, and the latter are left vacant [64].

$LiKSO_4$ is an interesting case. Five phase transitions are known. Three are at low temperatures [65], while the high-temperature ones occur at 709 K and 964 K, and the melting point is at 996 K [66]. The phase sequence is hexagonal–orthorhombic (pseudo-hexagonal)–hexagonal in the range from room temperature to the melting point [6, 67]. The transition enthalpy is 8.1 kJ/mole at 709 K [68], while it is much smaller at 946 K [69]. The electrical conductivity increases by a factor of 20 at the first transition, while the jump in conductivity is much smaller at the second transition [70]. The activation energy is 1.65 eV over a large fraction of the orthorhombic phase. The conductivity is of the order of 0.1 S/cm in the high-temperature phase [70], which is to be compared with 1.1 S/cm above the melting point [71]. The enthalpy of melting is considerably larger than the enthalpy of any solid-solid transition [72]. It has been suggested that the large conductivity at high temperatures is due to a "paddle-wheel" mechanism [70]. However, another alternative is a situation similar to the above-mentioned solution of Li^+ in Na_2SO_4-I. Thus, it is known that the Li^+ and K^+ ions occupy different sites, and that two lattice sites are available for each Li^+ ion in the high-temperature phase [70]. Furthermore, there is a considerable solid-solubility for Li^+ ions in the two highest phases, while there is no solid-solubility for K^+ ions in either of these phases [66]. A further study

of the cation transport mechanism in $LiKSO_4$ might be extended to include $LiRbSO_4$ and $LiCsSO_4$, which melt at 1017 K and 1013 K, respectively, and which do not show any solid-solubility for Li^+ [73].

The polymorphism of sodium thiosulphate, $Na_2S_2O_3$, has been studied by von Benda and von Benda [74]. A monoclinic phase, space group $P2_1/c$, is stable at room temperature. It transforms to a trigonal structure at 603 K, which is converted to a bcc phase at 661 K. The transition enthalpies are about 21 kJ/mole and 3 kJ/mole, respectively. Their sum is 24 kJ/mole, which can be compared with an enthalpy of 24.7 kJ/mole for the trigonal-bcc transition of $LiNaSO_4$ [68]. The coincidence might be fortuitous, since the accuracy of the measured enthalpy is not as good in the thiosulphate case as for the sulphate study. It is not possible to determine any enthalpy of melting, since $Na_2S_2O_3$ decomposes rapidly at temperatures above 715 K.

There are striking similarities between the bcc phases of $LiNaSO_4$ and $Na_2S_2O_3$ concerning line intensities of the X-ray powder diffraction pattern. The electrical conductivity of $Na_2S_2O_3$ is 0.325 S/cm at 673 K, and the activation energy $Q(\sigma T)$ is 0.33 eV. As a comparison, an extrapolation gives 0.28 S/cm for $LiNaSO_4$ at 673 K; the $Q(\sigma T)$ is 0.44 eV. There is no reason to doubt that the cation transport mechanism is essentially the same for these two bcc phases. Regarding the trigonal phase of $Na_2S_2O_3$, the conductivity is 0.11 S/cm at 623 K, and $Q(\sigma T)$ is 0.69 eV. (The extrapolated conductivity of bcc $LiNaSO_4$ is 0.17 S/cm at 623 K.) The high conductivity is explained by a dynamic model where the oscillation of the $S_2O_3^{2-}$ tetrahedra creates conduction pathways for the sodium ions [74].

Some chloroaluminates and -ferrates, $MXCl_4$ ($X = Al, Fe; M = Li, Na$) have attracted attention due, inter alia, to their electrical properties on both sides of the melting point. $LiAlCl_4$ and $LiFeCl_4$ melt at 419 K and 423 K, respectively [75, 76]. They are ionic conductors, with activation energies of 0.47 eV and 0.78 eV, respectively, in the region below 378 K. There is a rapid increase in the conductivity in the interval above the latter temperature. The two lithium compounds are monoclinic with the space group $P2_1/c$, i.e. they are isostructural. A solid solution has been obtained where the conductivity depends on the degree of ordering [77]. $NaAlCl_4$ melts at 426 K, and the electrical properties are similar to those of $LiAlCl_4$ [75]. $NaAlCl_4$ is orthorhombic with the space group

$P2_12_12_1$ [78]. The premelting of the two chloroalumi- nates has been studied by means of X-ray diffraction, differential scanning calorimetry and NMR [78]. It is concluded that the librational or rotational motions of the $AlCl_4^-$ groups are not continuous but are in- stead characterized by a discontinuous reorienta- tional movement, jumping from one stable position to another. The conductivity of Na^+ and Li^+ within the $AlCl_4^-$ ion lattice is not considered to be due to a con- ventional vacancy mechanism. Rather, the cations move whenever there is enough collective flexibility in the structure. The high ionic conductivity below the melting point is thus due to a liquidlike behaviour [78].

There are many other systems with polyatomic an- ions where large cation conductivities have been ob- served. I will give some examples without going into detail concerning the ion migration mechanism.

The conductivity of Na_3NO_3 shows a pronounced increase in the range 503 K–520 K [79, 80]. This has been interpreted as being due to the rotation of NO_2^- anions. This is, indeed, very likely. However, one should need to study also other properties than the structure and the conductivity in order to learn more about the details of the transport mechanism. Perhaps Na_3NO_3 has more in common with the chloroalumi- nates and -ferrates discussed above than with the plas- tic sulphate phases.

The cubic high-temperature phase of Na_3PO_4 shows a large solid solubility for aliovalent ions, and many conductivity studies have been performed, see e.g. [80–82]. The solid solubility of Na_2SO_4 is up to 70 mole% in this phase. The situation is similar for the system Na_3AlF_6-Na_2SO_4 [80, 81]. Based on the evi- dence available so far, cations appear to migrate by the same vacancy mechanism in the two cubic phases Na_3PO_4 and Na_3AlF_6 as in the hexagonal high-tem- perature sulphate phases Na_2SO_4, $LiKSO_4$ etc.

While the above-mentioned sodium phosphate-sul- phate system has attracted much interest, there have to my knowledge been only three investigations of Li_3PO_4-Li_2SO_4 [83–86]. There are some remarkable differences between the two systems. For example, up to 70 mole% of Na_2SO_4 is soluble in the cubic high- temperature phase Na_3PO_4, while only about 10 mole% of Li_2SO_4 can be dissolved in ortho- rhombic Li_3PO_4. On the other hand, up to 70 mole% of phosphate is soluble in fcc Li_2SO_4 [84].

The mentioned extremely high solubility of Li_3PO_4 in fcc Li_2SO_4 is found at 1394 K, which is 260 K

higher than the melting point of fcc Li_2SO_4. Other- wise, the solid solubility of anions is moderate in fcc Li_2SO_4. It is slightly less than 4 mole% for Li_2WO_4 [39] and 10 mole% for Li_2CO_3 [87]. The conductivity of the cubic sulphate phase decreases significantly when the concentration of the solute anion is in- creased. This occurs independent of whether phos- phate [84] or tungstate [39] is dissolved. These obser- vations are in good agreement with the paddle-wheel model for ion migration in cubic lithium sulphate [84, 85].

While it is common that high-temperature phases are characterized by extended ranges of solid solubil- ity, deviations from stoichiometry are usually small for room-temperature phases, see e.g. the binary sys- tems Li_2SO_4-M_2SO_4 (M = Na, K, Rb, Cs, Ag) [5, 66, 73, 88], Li_2SO_4-Li_2CO_3 [87] and Li_2SO_4-Li_3PO_4 [84, 86]. Such diagrams are characterized by wide two- phase regions at low and intermediate temperatures (below some 500 to 800 K). Conductivity maxima have occasionally been reported for compositions with two-phase regions, but this should be attributed to the grain-boundary phenomena characteristic for "composite electrolytes" [84, 86, 87, 89].

11. Conclusions

It is characteristic for solid salts with polyatomic anions that various modes of librational, rotational and vibrational motion occur. One can expect that this behaviour of the anions affects the mobility of the cations. The high-temperature hexagonal phase of Na_2SO_4 discussed briefly in Sect. 10, above, is a good example of the by far most common case. It is obvious that the presence of a large number of vacancies is the essential condition for a high cation conductivity. It is difficult to say to what extent the conductivity of a pure or a doped sample actually is enhanced by anion rotation etc. This can hardly be determined by mea- suring the conductivities of different salts. Perhaps the problem could be attacked by a molecular dynamics study of Na_2SO_4 where one compares the normal sulphate with sulphate where the mass of the anion has been increased very much, cf. the study of lithium sulphate by Ferrario et al. [21]. They increased the mass of the sulphate ion by 6400 amu. This was done in two different ways, either by distributing the added mass evenly over the four oxygen atoms of by placing all the extra mass at the site of the sulphur atom. In

the first case both the translational and the rotational degrees of freedom are frozen, while only the translational motion is suppressed in the second case. The best choice seems to be $Li_{0.5}Na_{1.5}SO_4$ where $D(Na)$ has been measured at two temperatures: 0.23×10^{-5} cm^2/s at 803 K, and 0.36×10^{-5} cm^2/s at 865 K [63, 64]. This corresponds to an activation energy, $Q(Na)$ of 0.4 eV. Actually, this coincides with the $Q(Na)$ of fcc $Li_{1.5}Na_{0.5}SO_4$ and bcc $LiNaSO_4$. Concerning (hexagonal) phases where the number of vacancies is large due to partial substitution with Li^+ or M^{2+}, it is of some interest that the upper limit for the conductivity and for the cation diffusion coefficients is some 25% of the values for the plastic cubic phases, cf. Table 1 in [63].

Let us go over to the cases where the cation mobility is very high also in the pure salt, i.e. our plastic sulphate phases (probably including $Na_2S_2O_3$), Na_3NO_3 and a couple of chloroaluminates and -ferrates. It seems evident that anion rotations/librations enhance the cation mobilities in all these cases, but there are clear differences between the plastic sulphates and the other mentioned materials. Thus, when dealing with transition enthalpies etc., it seems reasonable to consider the plastic phases to be more "liquid-like" than the other ones. It is a matter of taste

whether one should use the "paddle-wheel" as a cover for all processes where lattice vacancies are not required for obtained a mobility enhancement, or one should talk of a "paddle-wheel" mechanism only when dealing with the plastic phases. Personally, I think we should leave this matter open until we have a better knowledge of the transport mechanisms in the different phases.

When we introduced the "cogwheel" and "paddle-wheel" concepts we took it for granted that the transport processes were complicated, and that several of the contributions were enhanced. This has been confirmed by MD and RMC. Thus, we prefer not to speak of "the essence of the paddle-wheel" when discussing the fraction D_{reor} obtained by the MD simulations [21] or the corresponding contributions in the RMC study [1].

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