On the High Ionic Conductivity of Solid Solutions of Lithium Sulphate in Hexagonal Sodium Sulphate Na_2SO_4 (I)

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Solid solutions of Li_2SO_4 in the high-temperature phase Na_2SO_4 (I) have a much higher conductivity than expected. Diffusion and electromigration experiments show that both Li^+ and Na^+ ions are very mobile. It is concluded that the Li^+ ions go into interstitial positions of the type $(1/2, 0, 0)$, while vacancies are created in the Na^+ lattice.

The high-temperature phase of Na_2SO_4 has a high solubility for many other cations. As expected, the addition of di- and trivalent cations causes a pronounced increase of the ionic conductivity [1–4], but this is also the case when Li_2SO_4 is added [5, 6]. E.g. at 873 K the electrical conductivity is 0.002 S/cm for pure Na_2SO_4 [7], 0.29 S/cm for $Li_{0.5}Na_{1.5}SO_4$ [6] and 0.08 S/cm for $Mg_{0.25}Na_{1.5}SO_4$ [4]. Furthermore, an electromigration experiment has been performed for $Li_{0.4}Na_{1.6}SO_4$ [8], and the mobility was found to be 55% higher for Li^+ than for Na^+. Cation diffusion has been studied in $Li_{0.5}Na_{1.5}SO_4$ by Bengtzelius [9]: $D(Na)$ was 0.23×10^{-5} cm^2/s at 803 K and 0.36×10^{-5} cm^2/s at 865 K. This corresponds to an activation energy $Q(Na)$ of 0.4 eV. It may be fortuitous, but this coincides with the $Q(Na)$ of f.c.c. $Li_{1.5}Na_{0.5}SO_4$ and b.c.c. $LiNaSO_4$ [10].

The abovementioned pronounced conductivity-increases are a strong indication that vacancies are created in the Na^+ lattice not only when aliovalent cations are added, but also when Li^+ ions are present [11]. It is the purpose of this paper to see whether this is plausible according to X-ray structure data.

Na_2SO_4 (I) has the space group $P6_3/mmc$ [12, 13] with $a = 5.444$ Å, $c = 7.347$ Å, $Z = 2$ and $V = 188.6$ Å^3 at 693 K. There are two positions for Na^+ ions, cf. Figure 1. One is on the c-axis with coordinates $(0, 0, 0)$ and $(0, 0, 1/2)$, etc. The other position has coordinates of the type $(1/3, 2/3, 3/4)$ and $(2/3, 1/3, 1/4)$, etc. All sodium positions of both types are fully occupied. S is at $(1/3, 2/3, 1/4)$ and $(2/3, 1/3, 3/4)$, etc. i.e. they are straightly above or below those Na-positions that are "inside" the unit cell.

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The confidence is not quite as good concerning the oxygen positions. However, it seems evident that three oxygens are practically in a plane parallel to the $a-a$ plane and rather close to $c = 1/4$ or $3/4$. These oxy-
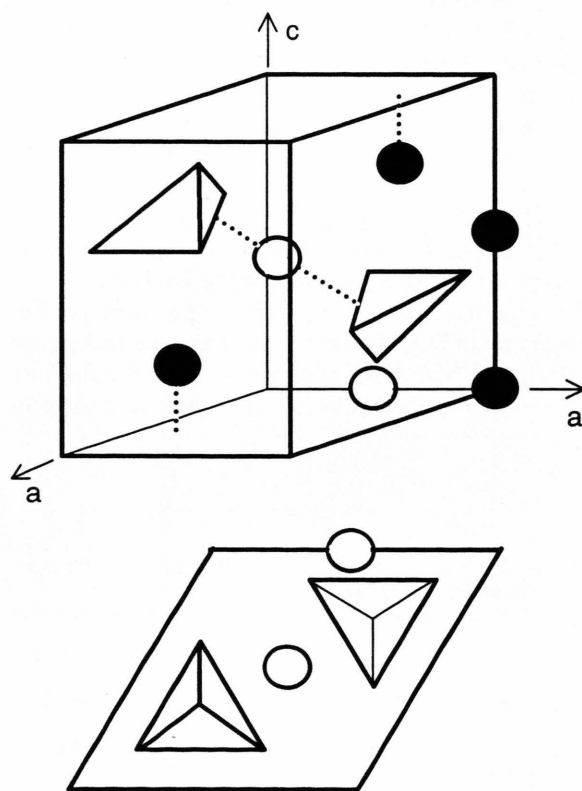

Fig. 1. A schematic representation of the hexagonal unit cell. The sulphate groups are shown as tetrahedrons, sodium ions as filled circles and the proposed interstitial positions as open circles. The sulphates are distributed statistically between "up" and "down" directions. Only a representative number of cation positions is shown.

gens have their largest vibrational motion in the c-direction. According to the most common opinion, two sides of the oxygen triangle are parallel to the a-axis of the cell. There is an excess of this type of oxygen positions. They are "mirrored" above or below the plane $c = 1/4$, and it should be this fact that results in the large vibrational amplitude in the c-direction.

The remaining 25% of the oxygen atoms are close to the threefold symmetry line through the SO_3 plane, in parallel with the c-axis. The orientation is such that the sulphate ions are equally divided between the directions "up" and "down". It seems reasonable that the top of the tetrahedron usually points in the direction that is not occupied by Na. There is a surplus also of these oxygen positions, with a star-shaped distribution around the symmetry axis.

The average interatomic distances of the structure can be summarized: Na–O 2.79 Å for Na on the c-axis and 3.05 Å inside the unit cell. The expected Na–O for 6-coordination is 2.25–2.78 Å [14]. The smallest Na–Na becomes 3.64 Å.

The only vacant site in the structure seems to be of the type $(1/2, 0, 0)$. There are six such positions of the type 6 g [14] per unit cell with the coordinates $(1/2, 0, 0)$, $(0, 1/2, 0)$, $(1/2, 1/2, 0)$, $(1/2, 0, 1/2)$, $(0, 1/2, 1/2)$, and $(1/2, 1/2, 1/2)$. They are all crystallographically equal except for the effects caused by the oxygen disorder. Thus there are in total three vacant positions per formula unit of SO_4. These positions are at a reasonable distance to both types of surrounding oxygens. Thus, the distance is abot 2.21–2.50 Å to those four oxygens

which are located in planes lying parallel with the a–a plane. Concerning the other type of oxygens, the distance is about 2.19 Å if the threefold symmetry axis is favourably oriented, i.e. if it is tilted away from the vacant position, but otherwise 1.42 Å. The expected Li–O distance is 1.86–2.05 Å if 4-coordinated, or 2.00–2.41 Å if 6-coordinated [14]. Thus, a possible introduction of Li in the considered positions should cause a certain tilting of neighbouring SO_4 tetrahedrons.

Na_2SO_4 (I) is isostructural with the high temperature phases of Ag_2SO_4, K_2SO_4, Rb_2SO_4, and Cs_2SO_4. While the solid solubility of Li is 46.5 mole% in Na_2SO_4 [15–17], it is 26 mole% in Ag_2SO_4 [18], 2–3 mole% in K_2SO_4 [17, 19] and not detectable (upper limit 2 mole%) in Rb_2SO_4 and Cs_2SO_4 [16, 17]. Thus, a pronounced conductivity enhancement due to doping with lithium can be expected to occur also in silver and potassium sulphate.

As said in the introductory section the activation energy for diffusion of sodium ions is nearly the same in Na_2SO_4 (I) as it is in the two cubic phases Li_2SO_4 and $LiNaSO_4$. A discussion of ion transport mechanisms in these two cubic phases will appear elsewhere [20].

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