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BRIEF COMMUNICATIONS

Cation Transport Mechanisms in High-Temperature Rotor Phases of Sulfates

ARNOLD LUNDÉN

Department of Physics, Chalmers University of Technology, S-412 96 Göteborg, Sweden

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Several high-temperature sulfate phases are plastic crystals, i.e., rotor phases. Their electrical conductivities are several orders of magnitude higher than those of "ordinary" salt crystals near the melting point. Secco has invoked a percolation-type mechanism rather than the "paddle-wheel mechanism." The electrical conductivity of solid solutions of tungstate in lithium sulfate has been suggested as a "crucial experiment" for choosing between these two mechanisms. A comparison is made of *all* experiments of this type performed so far for the range 2 to 50 mol% tungstate. A zoning experiment is presented in support of the Li_2SO_4–Li_2WO_4 phase diagram determined by Gunawardane *et al.* (*Br. Ceram. Trans. J.* **88**, 45 (1989)). A single-crystal neutron diffraction study of fcc Li_2SO_4 strongly supports the paddle-wheel mechanism. © 1993 Academic Press, Inc.

Introduction

One can distinguish between two groups of high-temperature phases of alkali sulfates by an examination of mechanical properties, thermal properties, and ion transport properties (*1–4*). Thus, fcc Li_2SO_4, bcc $LiNaSO_4$, bcc $LiAgSO_4$, and noncubic $Li_4Zn(SO_4)_3$ are considered as plastic crystals with ionic conductivities several orders of magnitude higher than those of "ordinary" high-temperature phases, among which hexagonal Na_2SO_4 has been studied most extensively. The self-diffusion coefficients of mono- and divalent cations are only moderately influenced by the ionic radii (*4*). This fact could be explained by the "paddle-wheel model" (originally named the cog-wheel model) for ionic transport (*5*). This model has been further supported by neutron and X-ray powder diffraction studies (*6*), and by a single-crystal neutron diffraction study (*7*).

It has, however, been claimed by Secco and co-workers that the observed extreme enhancement of the ionic conductivity should instead be due to a "a percolation-type mechanism where 'free volume' in the lattice framework plays a predominant role" (*8–10*). There have been some objections to Secco's proposals (*11–13*).

The "percolation-type" mechanism was first described in some detail (*9*) in 1992. I wish to draw attention to three investigations that had not been published when Secco submitted his latest paper.

Additional Support of the Phase Diagram

Concerning the system Li_2SO_4–Li_2WO_4, there are some discrepancies between (*9*) and the published phase diagram (*14*).

It was demonstrated by us in 1965 that a zone refining technique can be applied at a solid–solid transition. Thus, it was confirmed that both Li^+ and Ag^+ ions are very mobile in fcc Li_2SO_4 (*15*), and that the transition temperature of $^6Li_2SO_4$ is about 0.08°C

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lower than that of $^7Li_2SO_4$ (*16*). (Due to a miscalculation the difference is reported to be 0.7°C in Ref. (*16*).) In a third experiment on a sample of composition $Li_{1.96}K_{0.04}(SO_4)_{0.98}(WO_4)_{0.02}$ a zone was passed once at a rate of 0.45 mm/h (*17*). The unexpected result was that both K^+ and WO_4^{2-} were enriched. The plausible explanation is that the zone was molten. This is barely possible according to the Li_2SO_4–K_2SO_4 phase diagram that was reported a few years later (*18*), but when the phase diagram of Li_2SO_4–Li_2WO_4 appeared (*14*), it was evident that the composition $Li_{1.96}K_{0.04}(SO_4)_{0.98}(WO_4)_{0.02}$ had a low melting point. This supports the conclusion that the solubility of Li_2WO_4 in Li_2SO_4 is low.

The Electrical Conductivity of Sulfate-rich Mixtures

It has been repeatedly emphasized (*8–10*) that the addition of some tungstate to cubic lithium sulfate would reduce the conductivity if the paddle-wheel model were valid, but would increase it if the percolation model held. The results in the vicinity of 600°C are compared in Table I for five investigations. The trend is clear for the three independent studies made with a U-cell (*19–21*). For the solid solution the conductivity is lowered when the tungstate concentration is increased. There is a pronounced change in going from a solid solution to a solid–liquid mixture. In the two-phase region the conductivity increases on going from 4% to 10%. For temperatures below 581°C these compositions correspond to solid–solid two-phase regions (*14*).

In addition to the experiments using U-cells, there are two studies with rather thin and wide pellets (*8*, *10*) for which the significantly higher conductivity ratios spread from 2.1 to 24 depending on how the sample had been prepared and on the frequency. The conductivity values and the activation energies have been discussed previously (*11*). The choice of the sample size has been commented on (*12*).

TABLE I

MODIFICATION OF IONIC CONDUCTIVITY BY THE ADDITION OF Li_2WO_4 TO Li_2SO_4

Li_2SO_4 (mole%)	σ_i/σ_0	Phase	Remark[a]	Ref.
2	0.84	fcc		(*19*, *11*)
2.5	0.83	fcc		(*20*)
3.0	0.81	fcc		(*20*)
3.5	0.79	fcc		(*20*)
4.0	1.02[b]	fcc + liq.		(*20*)
5.0	1.10	fcc + liq.		(*21*, *11*)
10.0	1.16	fcc + liq.		(*21*, *11*)
10.0	4.2	fcc + liq.	comp. 1 kHz	(*8*)
10.0	12	fcc + liq.	unco. 1 kHz	(*8*)
10.0	24	fcc + liq.	unco. 10 kHz	(*8*)
10.0	3.5	fcc + liq.	comp.	(*10*)
20.0	2.1	fcc + liq.	comp.	(*10*)
50	1.39	liq.	extrapol.	(*19*, *11*)

Note. Since five independent studies are compared the ratios are between the conductivities of the doped samples and pure Li_2SO_4. Temperature is 600°C (578°C for Ref. 11).

[a] Comp. = compressed polycrystalline sample; unco. = uncompressed solidified sample.

[b] There is an error in Table 1 of Ref. (*20*). The conductivity at 600°C is 1.16 S/cm for a sample containing 4 mole% Li_2WO_4.

Secco has made many comparisons with other studies (*9*). However, nearly all of these refer to regions for which the paddle-wheel mechanism has not been invoked in the original papers.

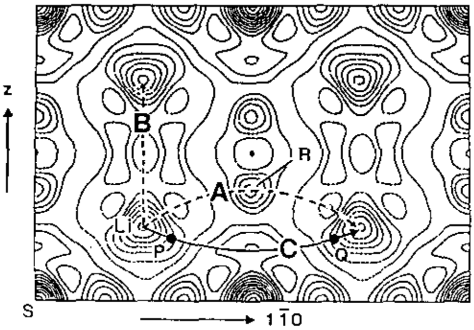

FIG. 1. Single crystal neutron diffraction study of fcc Li_2SO_4 (*7*). The observed Fourier synthesis of the nuclear densities in the 110-plane is shown. Three possible lithium conduction pathways (A, B, and C) are discussed in detail elsewhere (*7*).

A Neutron Diffraction Study of a Single Crystal

Figure 1 shows the nuclear densities in the 110 plane, as obtained from a single-crystal neutron diffraction study of cubic Li_2SO_4 (*7*). It was not possible to refine a model with any degree of lithium occupancy at the octahedral position $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. This speaks against percolation mechanisms, in which Li^+ ions jump from a tetrahedral position via an octahedral one to a vacant tetrahedral position. The best refinement results were obtained for a model where about 90% of the Li^+ ions were in tetrahedral 8*c* sites $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$, while the remaining 10% were distributed in spherical shells of radius 2.8 Å surrounding the sulfate ions.

The three lithium conduction paths shown in Fig. 1 are discussed elsewhere (*7*); it is concluded that only path C is in agreement with the single-crystal neutron diffraction study. Thus, a Li^+ ion in an 8*c* position P makes a jump into the spherical "lithium shell," and jumps from this shell into a vacant 8*c* position Q. For these jumps the probability is slightly higher for a light isotope than for a heavy one, which has been verified in studies of electromigration (*22*), electrical conductivity (*23*), and self-diffusion (*24*).

The paddle-wheel mechanism that has been confirmed by the neutron diffraction study is in agreement with the early finding that the mono- and divalent cation self-diffusion coefficients are only moderately influenced by the ionic radii (*4*). The studies of many other properties are compatible with what can be expected on basis of the paddle-wheel mechanism (*2*). To date, no other model has been presented which is capable of explaining all kinds of properties of the discussed group of plastic inorganic crystalline high-temperature phases.

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