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Fast ion conductors with rotating sulphate ions


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1. Introduction. — During slightly more than a decade, it has been discovered that a very large number of ionic solids have a high ionic conductivity in a region, which can cover several hundreds of degrees. Such compounds are called solid electrolytes provided that the electronic conductivity is negligible in comparison with the ionic, while both are comparable in mixed conductors. These materials can be divided into classes which differ in certain aspects. Thus the sulphate phases studied in our laboratory are characterized by having a high mobility for all mono- and divalent cations for which diffusion studies have been made [1], see table I, while for other classes the number of very mobile species is much more restricted. Our recent studies of sulphates have aimed at explaining the transport mechanism and at comparisons of properties in order to find out what is characteristic of a solid electrolyte. We shall here report on X-ray and neutron diffraction studies as well as on Brillouin scattering (inelastic scattering of light) and on rheology studies.

2. X-ray and neutron diffraction studies. — Several authors have studied the structure of sulphate phases by means of X-ray diffraction [2-5]. In addition to fcc Li2SO4 there are bcc phases with the approximate compositions LiNaSO4, LiAgSO4 and Li2Ag(SO4)2 I and a non-cubic phase Li2Zn(SO4)3 on which work is in progress. Characteristic of all phases is that the X-ray diffraction patterns show a very low number of lines which, however, are sharp (see Fig. 1). Neutron diffraction studies have also been made for the fcc phase, using the high-flux powder diffractometer D2 at Grenoble, France, and the DIDO triple-axis instrument at Harwell, England, for pure Li2SO4 [6] and the triple-axis instrument TAS 4 at Risø, Denmark, for a sample containing 20% Ag2SO4. The Bragg peaks are now superimposed on a high background consisting of at least three wide humps (see Fig. 2). The diffraction patterns are essentially the same for pure Li2SO4 and the mixture, indicating that the location and the transport mechanism is...
about the same for both Li\(^+\) and Ag\(^+\) ions in this phase. This is expected from the diffusion data, table I.

The use of the energy-resolving triple axis spectrometers rules out the possibility that the background might be due to inelastic scattering. The high intensity of the background can only be due to oxygen atoms. Least-squares refinement methods were used to analyse the pure Bragg-reflexion part of the diffractogram [6]. The sulphate ion is situated at the origin of the face-centered-cubic structure with the oxygen atoms essentially rotationally disordered around the sulphur. The isotropic temperature factors are large, which suggests that the cations occupy a statistical distribution of sites instantaneously displaced from (1/4, 1/4, 1/4) in short range correlation with the instantaneous orientations of the surrounding sulphate ions.

3. Brillouin scattering. — Brillouin scattering, i.e. inelastic scattering of light due to interactions with phonons (thermal sound waves), is a well-known method for structural studies of liquids and solids. Since the solid electrolyte phases have several properties that resemble liquids rather than solids, we considered it of interest to extend our previous studies of molten salts to cover both solid and molten lithium sulphate [7]. Figure 3 shows that the Brillouin spectra of the two phases differ considerably. The very intense central line in the solid phase is due to elastic scattering of light by defects. Furthermore, a transverse mode typical of a solid appears in the fcc phase. The longitudinal mode is shifted further away from the central peak in the solid phase than in the liquid. This means that the hypersonic velocity is lower in the melt than in the solid. In both phases the velocity decreases smoothly with increasing temperature, but with a sharp drop of about 35% at the melting point. On the other hand, the refractive index, another optical property studied by us, decreases only 0.3% when the salt melts.

In the experiments performed so far the measurements started in the melt, and the temperature was then lowered slowly through the freezing point, whereupon the measurements were continued with the sample holder in the same position through the whole range down to the transition to the monoclinic phase at 575 °C. We also made an experiment where the sample holder was rotated at constant temperature. It was found that the frequency shift varied periodically with the rotation angle, which indicates that the scattering volume is comparable with, or less than the volume of a single crystal [7]. In order to obtain additional information it is necessary to work with oriented single crystals and a high resolution interferometer. Work is in progress along these lines.

4. Rheology. — The transition at 575 °C between the monoclinic and the fcc phases is characterized by an extremely high latent heat, 23.5 kJ/mol, while
the heat of melting is only 7.4 kJ/mol [6]. A first order phase transition with a high heat of melting is typical not only of a large number of solid electrolytes, but also of another class of substances called plastic crystals. We have found that bcc AgI and fcc Li$_2$SO$_4$ show plastic crystal behaviour. Thus, they are both thixotropic, and the relaxation time for Li$_2$SO$_4$ is 8.4 hrs at 781 °C [8].

Stress relaxation studies show that AgI, Li$_2$SO$_4$ and Li$_2$SO$_4$-K$_2$SO$_4$ mixtures follow the general pattern of most plastic substances which has been established by a great number of investigators: The activation volume for flow is inversely proportional to the initial shear stress. This proportionality is improved if a constant term, the internal stress, is subtracted from the applied stress. In most work reported up till now the proportionality constant is of the order of 10, while in our work on Li$_2$SO$_4$ mixtures the constant is about 5. The theoretical work considering this observed proportionality [9] uses a statistical approach and cannot include specific properties of the different relaxing substances which should be responsible for the different values of the proportionality constant.

The internal stress mentioned above is often considered to be constant. Careful analysis of the Li$_2$SO$_4$ data shows, however, a weak temperature dependence which can be described by a linear equation in $T$ in the range 1010-1110 K.

5. General conclusions. — fcc Li$_2$SO$_4$ is the first example of a rotator phase found among solid electrolytes, and there is reason to assume that the other sulphate phases also are rotator phases. In such a phase the high degree of spherical delocation of the sulphate ions can be considered the cause of all the unusual properties, including the high cation mobilities. Further comparisons with other types of substances, including other solid electrolytes, should give a better understanding of how physical properties depend upon structure.

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