COMMUNICATION NO. 179
OF THE
CENTRAL LABORATORY

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Reprinted from
Physica **30** (1964) 1682-1688

CENTRAL LABORATORY T.N.O., 132 JULIANALAAN, DELFT, THE NETHERLANDS

Van Beek, L. K. H.
1964

Physica 30
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PROTON MOBILITIES IN SINGLE CRYSTALS OF $Li_2SO_4 \cdot H_2O$

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Synopsis

Proton mobilities in single crystals of $Li_2SO_4 \cdot H_2O$ are derived from its dielectric behaviour between 0.01 and 10 Hz and from dc transients. Space charge effects were appreciable only in samples cut perpendicular to the crystallographic *b*-axis. The dielectric effects of space charge are discussed for a simple model, in which the sample with space charge layer is considered as a capacitance in series with a resistance. The mobilities calculated are of the order 6×10^{-7} m^2/Vs.

1. In a recent paper, proton mobilities in $Li_2SO_4 \cdot H_2O$ were derived from dielectric measurements at low frequencies [1]). A dielectric loss maximum around 0.2 Hz, which was attributed to space charge polarization, was observed in samples prepared by compression of polycrystalline powders. Since proton conduction had been established [2]) in $Li_2SO_4 \cdot H_2O$, the polarization was ascribed to protons and a mobility of about 10^{-5} m^2/Vs was calculated with the aid of Macdonald's theory [3]). The use of compressed samples, however, remains unsatisfactory, because it is impossible to tell whether the observed effects are real properties of the material; also, the way in which the theory should be applied is not completely clear in the case of compacted powders. Therefore, the measurements were repeated for single crystals, and the directional effect of conductivity was studied. In addition, the theoretical equations were clarified by consideration of a simple model.

2. *Experimental procedure.* Samples were cut with nylon thread from almost flawless big crystals both perpendicular and parallel to the crystallographic *b*-axis (the twofold axis). The size of the crystals permitted samples with a surface area of 6–8 cm^2 to be obtained. Sample faces were made flat and parallel by grinding with emery powder and water, followed by polishing with emery powder and silicone oil. Next, the faces were washed with acetone and provided with silverpaint electrodes (conductive coating Nr. 3040, Waldman).

Dielectric measurements between 0.01 and 10 Hz were carried out with

a low frequency bridge based on the design by Nakajima and Kondo [4]). The balance point of the bridge below 0.2 Hz was determined by using a sensitive recorder (Micrograph, Kipp). Measurements above 60 Hz were performed with a Schering bridge (Rohde and Schwarz). The samples were measured in a condenser without guard ring. Corrections were applied for the empty space between the plates, and for edge capacitance. The equipment was tested and the corrections were verified by measuring a pure polymethylmethacrylate with silverpaint electrodes; the results were almost exactly the same as those recently reported by Scheiber [5]). Direct current transients at 50 V were read from the scale of a microammeter (Hewlett-Packard, model 425A).

3. *Dielectric measurements.* 3.1. Theory. Macdonald's theory of ac space charge polarization is a generalization and extension of an earlier theory developed by Jaffé [6]). Both theories consider a material with blocking electrodes in which the charge carriers can move freely. Under the influence of an electric field, space charge layers will be built up at the electrodes. The thickness of these layers will be of the order of a Debye length L_D. The presence of a space charge layer of thickness L_D that is smaller than the sample thickness d, causes the capacitance of the sample to increase from its real value C to an apparent value

$$C^* = Cd/2L_D. \tag{1}$$

The factor of 2 follows from the assumption that there are space charge layers at both electrodes. Eq. (1) shows that the dielectric constant at very low frequencies is not the real static dielectric constant κ_s, but an apparent value

$$\kappa_s^* = \kappa_s d/2L_D. \tag{2}$$

The double layer can be considered as a capacitance in series with a resistance R, where $\rho = RA/d$ is the resistivity of a sample and A is its surface area. The system has a characteristic time $\tau = RC$. With the aid of eq (1), and making use of the well-known relation $C = \varepsilon_0 \kappa_s A/2L_D$, where $\varepsilon_0 = 8.85\ pF/m$ is the dielectric constant of vacuum, we find:

$$\tau = \mathrm{d}\varepsilon_0 \kappa_s / 2\sigma L_D \tag{3}$$

where $\sigma = 1/\rho$ is the ionic conductivity of the material. Eqs (2) and (3) are identical with results obtained by Macdonald in his much more general treatment [3]). The time τ can, in principle, be determined in two ways, from dc transients and from dielectric loss measurements. A dielectric loss peak will appear at a critical frequency

$$\nu_m = 1/2\pi\tau. \tag{4}$$

There remains some doubt about the correct expression for L_D. Considering Bjerrum faults as the source of charge carriers, Onsager and Dupuis derived for ice [7])

$$L_D^2 = \varepsilon_0(\kappa_s - \kappa_\infty)\kappa_\infty \, kT/2\kappa_s q^2 N \tag{5}$$

where $q = 6.6 \times 10^{-20}$C is the charge of a Bjerrum fault, k = Boltzmann's constant, κ_∞ is the limiting dielectric constant at very high frequencies. Eq. (5) implies that when $\kappa_s \gg \kappa_\infty$, which is often the case, L_D is determined by κ_∞.

Another possibility is that protons move through the crystal, for example by a tunnelling mechanism. Then, according to Macdonald, $L_D^2 = D\tau_D$, where D is the diffusion constant related to the mobility μ through the Einstein relation $\mu/D = e/kT$, and $\tau_D = \varepsilon_0(\kappa_s - \kappa_\infty)/\sigma$ is the Debye relaxation time. Making use of the relation $\sigma = Ne\mu$, where N is the proton concentration, we find that in the second case L_D depends on κ_s rather than on κ_∞

$$L_D^2 = \varepsilon_0(\kappa_s - \kappa_\infty) \, kT/e^2 N. \tag{6}$$

The electronic charge $e = 1.6 \times 10^{-19}C$.

3.2. Results. An example of the observed dielectric dispersion is given in figs 1 and 2 for a sample 2.1 mm thick, and cut perpendicular to the b-axis. Along the crystallographic b-axis conditions for protonic conduction appear to be most favourable [2]). Fig. 1 shows the dielectric loss factor, κ'', as a

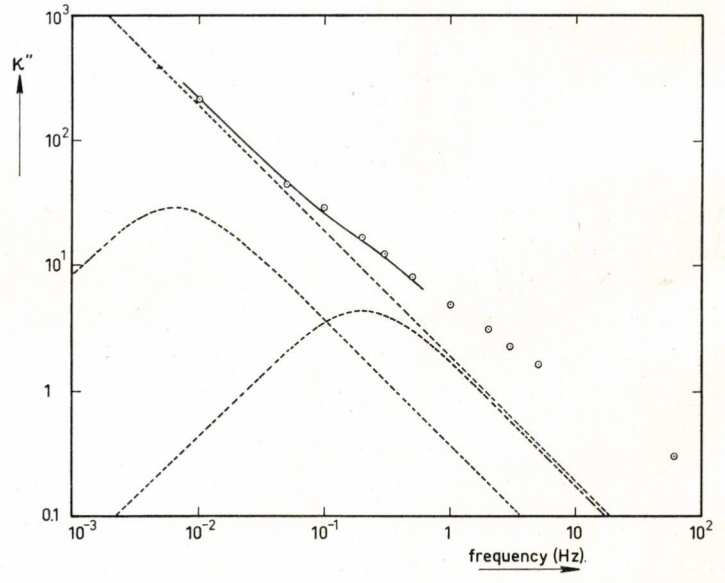

Fig. 1. Dependence of the loss factor of $Li_2SO_4 \cdot H_2O$ upon frequency. The dotted straight line represents conductivity loss. The solid curve is the sum of conductivity loss and the two loss peaks. The sample was 2.1 ,mm thick and $\perp$ b-axis.

function of frequency. Analysis of the low frequency part of the loss curve leads in all cases considered to a loss maximum at about 0.2 Hz, with a height of about $\kappa''_m = 4.4$, and limiting dielectric constants $\kappa_s = 22$ and $\kappa_2 = 13.2$. This maximum was found from analysis of the dielectric data by trial and error, and also by algebraic calculation of κ_s, κ_2, and ν_m from the experimental constants between 0.1 and 1 Hz. In the analysis, simple Debye equations are used

$$\kappa' = \kappa_\infty + \frac{\kappa_s - \kappa_\infty}{1 + \omega^2\tau^2} \tag{7}$$

and

$$\kappa'' = \frac{(\kappa_s - \kappa_\infty)\omega\tau}{1 + \omega^2\tau^2} \tag{8}$$

where $\omega = 2\pi\nu$, and τ is given by eq. (4). The maximum at 0.2 Hz was found to be independent of sample thickness and independent of crystallographic orientation. From eq (2) one would expect dependence on sample thickness and the absence of such an effect makes it unlikely that this maximum is caused by space charge polarization. No attempts will be made to interpret the maximum at 0.2 Hz in the present paper; we intend to give a further analysis of the dielectric behaviour of $Li_2SO_4 \cdot H_2O$ at a later stage.

Space charge effects occur in single crystals of $Li_2SO_4 \cdot H_2O$ at frequencies below 0.1 Hz, and apparently only in samples cut perpendicular to the *b*-axis. This conclusion can be conjectured from various observations. Firstly, a renewed ascent of the dielectric constant toward low frequencies is observed at 0.05 Hz and 0.01 Hz in all samples cut perpendicular to the *b*-axis. This observation eliminates the possibility that the loss below 0.1 Hz would be exclusively caused by dc conductivity. Unfortunately, 0.01 Hz is the lower limit of our measuring range; the dispersion cannot be followed to its completion. The dielectric data only show that there exists a dispersion region around 0.01 Hz, and while κ_s can be determined, κ_s^* can be derived only by algebraic calculation, using eq. (7), provided that ν_m is known.

A second obeservation indicating space charge formation is that the current decreases in time, when a steady voltage is applied. From this effect a characteristic time can be derived, which gives us the required value of ν_m. The transients, measured at 50 V, were analyzed with the relation

$$i = i_\infty + (i_0 - i_\infty) \exp(-t/\tau). \tag{9}$$

The results were reproducible, and the critical frequencies ν_m calculated from the experimental τ values by means of eq. (4) showed the expected dependence upon sample thickness. For example, samples 2.1 and 4.6 mm in thickness had ν_m values of 0.0064 ($\pm$ 0.0003) and 0.0026 ($\pm$ 0.0002) Hz,

respectively. In other words, the critical frequency is inversely proportional to the sample thickness, in agreement with eq (3). Therefore, the dispersion observed below 0.1 Hz appears to be indeed caused by space charge polarization. Making use of the ν_m values obtained from dc transients, we calcula-

TABLE I

Apparent static dielectric constants κ_s^*, static dielectric constants κ_s, next limiting dielectric constant κ_2, and optical dielectric constant [8]) κ_∞.

sample	d[mm]	ν_m[Hz]	κ_s^*	κ_s	κ_2	κ' (at 100 kHz)	$\kappa_\infty = n^2$
// b-axis	3.1	—	—	21.5	11.1	5.6	2.13
⊥ b-axis	4.6	0.0026	190	20.9	13.2	11.0	2.2
⊥ b-axis	2.1	0.0064	80	22.0	13.2	11.0	2.2

ted the κ_s^* values given in table I. From all evidence available, these values appear to be good approximations. As a further test, the dielectric constant as a function of frequency was calculated for the 2.1 mm sample from the Debye equation:

$$\kappa' = 13.2 + \frac{58}{1 + (\nu/0.0064)^2} + \frac{8.8}{1 + (\nu/0.2)^2}.$$

The resulting curve is indeed reasonably close to the experimental points.

Interestingly, attempts to move ν_m to frequencies above 0.01 Hz by preparing very thin samples ($\leqslant 1$ mm) failed. The space charge polarization effect seemed to have disappeared or, at least, had become so small that it could not be detected in view of the experimental accuracy.

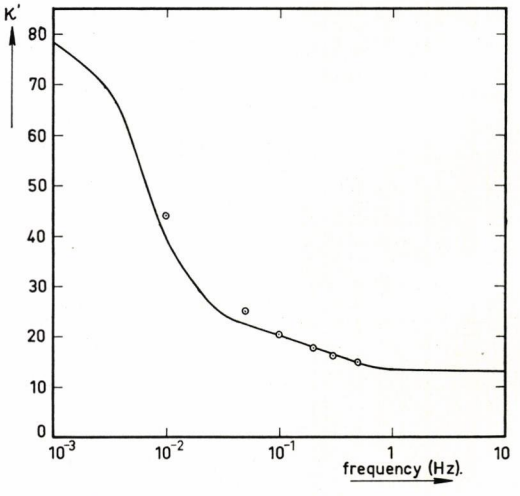

Fig. 2. Dependence of the dielectric constant of the sample of Fig. 1 upon the logarithm of frequency. The solid line is the calculated dispersion curve corresponding with the two loss peaks in Fig. 1.

In contrast with samples cut perpendicular to the *b*-axis, those cut parallel to the *b*-axis did not show appreciable space charge effects above 0.01 Hz. The absence of space charge effects made the samples parallel to the *b*-axis suitable for derivation of some general properties of the substance. A low frequency loss maximum at 0.2 Hz was observed in these samples, just as in the samples cut perpendicular to the *b*-axis. This observation is in line with the assumption that the peak at 0.2 Hz has no relation to space charge. The dc resistivity of these samples could be accurately determined and was found to be $1.0 \times 10^{10}\ \Omega$ m. Exactly the same value was derived from the dielectric loss factor at low frequencies, using the relation

$$\kappa''_\sigma = \sigma/2\pi\nu\varepsilon_0 \tag{10}$$

where κ''_σ represents conductivity loss owing to a dc conductivity σ. The same conductivity loss was found when in samples cut perpendicular to the *b*-axis space charge loss was subtracted from the values represented by the experimental curve. The dotted straight line in fig. 1 was obtained in this way. Apparently the same dc conductivity is present, whether there are space charge effects or not. Therefore, the dc conductivity cannot be ionic but must be ascribed to electrons or holes. This would be in agreement with another observation, namely that the current increases about one hundredfold as soon as the electrodes are no longer blocking ones; evidently the protonic current is then added to the electronic current.

4. *Discussion.* The occurrence of protonic conduction in $Li_2SO_4 \cdot H_2O$ was established by electrolysis experiments, and by chemical analysis of the gas evolved [2]). Ionic conduction is also suggested by currents decreasing in time at constant applied voltage, and by dielectric space charge effects, which were found both in compressed samples [1]) and in single crystals cut perpendicular to the *b*-axis. There is, however, a striking difference between the dielectric properties at low frequencies of single crystals and the previously studied compressed samples. Compressed samples had much higher dielectric loss (e.g. $\kappa_s^* = 380$, $\kappa_s = 105$) and the space charge loss maximum was found at 0.2 Hz. Matters were probably complicated by the existence of the other maximum at 0.2 Hz, which was now observed in single crystals, but which was probably obliterated by space charge loss in the compressed samples. Heterogeneity is suggested by the high value $\kappa_s = 105$, which may be explained for example by considering a many-layer model [9]). The fact that the space charge maximum was found at a frequency as high as 0.2 Hz also points to the effect of many superposed thin layers. Alternatively, space charge polarization owing to electrons cannot be ruled out. The compressed samples had Al foil electrodes which were stuck on the faces with some vaseline, and these electrodes may have been blocking to electrons.

The conduction mechanism is not known, and there is no simple way to decide between Bjerrum faults as in ice, proton tunnelling, or perhaps another mechanism. Rather arbitrarily we have chosen eq. (6) to calculate N from L_D, taking $\kappa_\infty = n^2$. Use of eq. (5) would give mobilities about ten times higher than the values given in table II. The Debye length L_D follows immediately from eq. (2). The mobility is calculated by making use of eqs (3) and (4) ,which lead to $\mu = \pi \nu_m d \varepsilon_0 \kappa_s / N e L_D$. The concentration, N, is given per m^3 and as a function of the total concentration of protons in a sample of 2.06 g/cm^3 density.

TABLE II

Derived values of Debye length L_D, mobility μ and proton concentration N in single crystals of $Li_2SO_4 . H_2O$

Sample	d[mm]	L_D[mm]	μ[m^2/Vs]	N[m^{-3}]	N (ratio)
$\perp$ *b*-axis	4.6	0.25	5.1×10^{-7}	3.4×10^{14}	$1 : 6 \times 10^{14}$
$\perp$ *b*-axis	2.1	0.29	6.6×10^{-7}	2.7×10^{14}	$1 : 7 \times 10^{14}$

The mobility in single crystals calculated in the manner described, is about fifty times smaller than that found in ice doped with *HF*. It is a little higher than the proton mobility in water, which equals [10]) 3.6×10^{-7} m^2/Vs.

Acknowledgement. The author wishes to thank Ir. H. A. Waterman (C.L.–T.N.O.) and Dr. A. Rose (R.C.A.Lab., Princeton, N.J., U.S.A.) for valuable discussions, which were very helpful for the clarification of the theory; Dr. W. F. de Jong (Crystallography Dept., Tech. Univ., Delft) and his staff for providing single crystals and for help and advice in cutting samples; Mr. W. F. H. Vasbinder and Mr. H. J. van der Vossen for excellent experimental assistance.

Received 14-3-64

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