NMR investigations of cation diffusion in some solids with antifluorite structure

M. Mousa, Y. Oei, H. Richtering

NMR investigations of cation diffusion in some solids with antifluorite structure

M. Mousa, Y. S. Oei and H. Richtering

Department of Chemistry, Ruhr University Bochum, F.R. Germany

Résumé. — Temps de relaxation spin-réseau et largeur de la raie de résonance de ^{7}Li et ^{23}Na ont été mesurés jusqu'à 800 °C pour Li_2S, Li_2O, Na_2S et Na_2O. La relaxation qui est due à la diffusion du cation est observée; ici dans Li_2S et Li_2O les interactions dipolaires et dans Na_2S et Na_2O les interactions quadrupolaires sont prédominantes. Rétrécissement des raies de résonance dû au mouvement est trouvé au-dessous de 300 °C. Pour Li_2S, Li_2O et Na_2S les fréquences de saut des cations sont déterminées dans les régions qui correspondent au désordre intrinsèque ou extrinsèque avec des énergies d'activation apparentes approximatives de 1,4 et 0,7 eV pour Li_2S, 1,3 et 0,55 eV pour Li_2O et 1,3 et 0,7 eV pour Na_2S. Les conductivités ioniques qui sont calculées à partir des dates rmn s'accordent avec les conductivités déterminées directement au mieux d'un facteur 3.

Abstract. — Spin-lattice relaxation rates and nmr linewidths of ^{7}Li and ^{23}Na have been measured up to 800 °C for Li_2S, Li_2O, Na_2S and for Na_2O. Relaxation due to cation diffusion is observed with predominant dipole interactions in Li_2S and Li_2O and quadrupole interactions in Na_2S and Na_2O. Motional narrowing occurs below 300 °C. For Li_2S, Li_2O and Na_2S cation jump frequencies in the regions of intrinsic and of extrinsic disorder are determined with apparent activation energies of about 1.4 and 0.7 eV for Li_2S, 1.3 and 0.55 eV for Li_2O and 1.3 and 0.7 eV for Na_2S. Ionic conductivities calculated from the nmr data agree with conductivities determined directly within a factor 3.

1. Introduction.

— Investigations of atomic transport in ionic crystals with antifluorite structure are scarce. By analogy with the fluorites a Frenkel type disorder of the cations and a comparatively high cationic conductivity is to be expected. For Na_2S such a behaviour has been demonstrated by Möbius *et al.* [1]. Since ^{7}Li and ^{23}Na are suitable for nmr-detection, we have measured nmr relaxation rates in Li_2S, Li_2O [2], Na_2S and Na_2O up to 800 °C in order to study the cationic diffusion. Such investigations do not require single crystals which were not available to us. In addition the electrical conductivity was determined in order to compare the results of the two methods. Pellets made from powdered material under pressure were used for these measurements. Because of their reactivity in the presence of moisture and the tendency of Li_2S and Na_2S to form polysulfides the purity of the materials used was not of as high a standard as achieved in the case of the alkali halides of CaF_2. Foreign anions were probably the most important impurities.

2. Materials and techniques of measurement.

— Li_2S was prepared from lithium metal (Merck) and a stream of dry H_2S in redistilled absolute ethanol [3]. The preparation of Li_2O has been described previously [2]. Li_2O as well as Na_2O are easily spoiled by reaction with quartz (used as container material) at elevated temperature if traces of moisture are present. Na_2S was prepared from $Na_2S.9\,H_2O$ (Merck) as described by Courtois [4]. Na_2O as commercially available (Merck) was carefully dried under vacuum at elevated temperature and treated with sodium metal. All substances were handled in a dry box and sealed in sample tubes of quartz under vacuum.

The spin-lattice relaxation rates were determined by standard pulse techniques with a Bruker spectrometer (BKR 321). Linewidths of the nmr absorption signals were recorded by a Varian wide-line spectrometer. The electrical conductivity of polycrystalline pellets was measured between platinum electrodes at 1 to 10 kHz with an impedance bridge (General Radio, model 1656). The pellets were annealed for several days between the electrodes in an inert atmosphere before reproducible results could be obtained.

3. Results.

— The spin-lattice relaxation rate $1/T_1$ for ^{7}Li in Li_2S as function of temperature exhibits a pronounced maximum. The position of the maximum is shifted to lower temperature with decreasing Larmor-frequency ω, the peak height is found to be proportional to $1/\omega$. This is the expected behaviour for relaxation caused by diffusion of Li^+ ions. At the temperature of maximum relaxation rate the mean jump frequency ν of these ions approximately equals

ω. For magnetic dipole interaction between the diffusing nuclei the following relation holds :

$$\frac{1}{T_1} = A \left\{ J(\omega) + 4 J(2 \omega) \right\} .$$

The constant A can be calculated from nuclear data of ^{7}Li. $J(\omega)$ and $J(2\omega)$ are spectral densities of the fluctuations in dipole interaction due to diffusion. These spectral densities have been calculated for several types of lattice diffusion by Torrey [5, 6] and Sholl [7]. They contain an nmr correlation time as a parameter and depend to some extent on the diffusion mechanism. The nmr correlation time τ is related to the mean jump frequency v by $(1/\tau) = 2.v.f.$ The nmr correlation factor f is introduced to account for the spatial and temporal correlation in a given mechanism [8]. Numerical values have been calculated by Wolf et al. [9] for small concentration of atomic defects. For diffusion via vacancies on nearest neighbour positions (mechanism 1) or on third nearest neighbour positions (mechanism 2) the numerical values are $f = 0.35$ and $f \approx 0.25$ respectively. The blocking of half the elementary cation cubes by the anions was taken into account in the case of mechanism 2. The jump distances for mechanism 1 and 2 are $r = d/2$ and $r = (d/2) \sqrt{3}$ respectively (d : lattice constant). From v and the mean jump distance r the cationic conductivity σ can be calculated by the Nernst-Einstein relation $\sigma . T \sim v.r^2$. Results are shown in figure 1. The data obtained from measure-
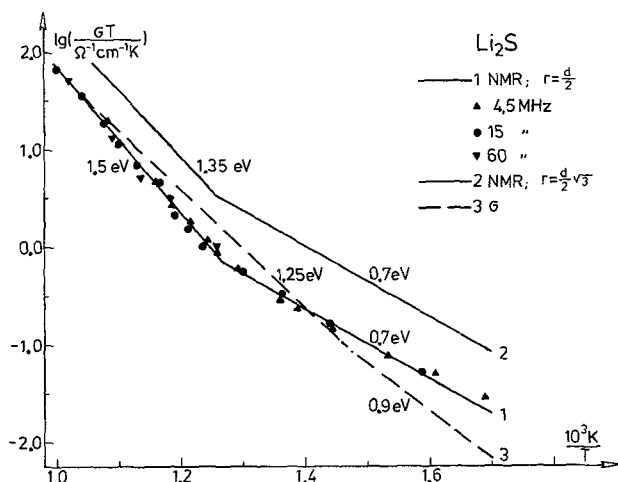

Fig. 1. — Cationic conductivity in Li$_2$S derived from ^{7}Li relaxation rates. — — — — : conductivity measured directly.

ments with three Larmor frequencies are explicitely indicated for mechanism 1 only. The Arrhenius plot exhibits two linear branches which are typical for extrinsic and intrinsic conduction. In the intrinsic region the measured conductivity is between the calculated curves for mechanisms 1 and 2 respectively. The nmr results show a smaller slope and exceed our measured conductivity considerably at low tem-

peratures. Huggins [10], however, has reported conductivity data in the extrinsic region, which are between the calculated curves in figure 1.

The agreement between calculated and measured conductivities is quite satisfactory if one takes into account that the experimental methods are fundamentally different, that uncertainties with the spectral densities remain, and that experimental difficulties exist with the conductivity measurements. It is not possible, however, to derive which diffusion mechanism is operative in Li$_2$S. Activation energies of about $\varepsilon_1 = 1.4$ eV for intrinsic disorder and of $\varepsilon_2 = 0.7$ eV for vacancy diffusion can be estimated.

Similar measurements have been performed for Li$_2$O. The most important impurity in this solid are probably OH$^-$ ions. The presence of the corresponding cation vacancies can be detected by the nmr measurements simultaneously with the determination of v [2]. Figure 2 shows nmr results for two diffe-
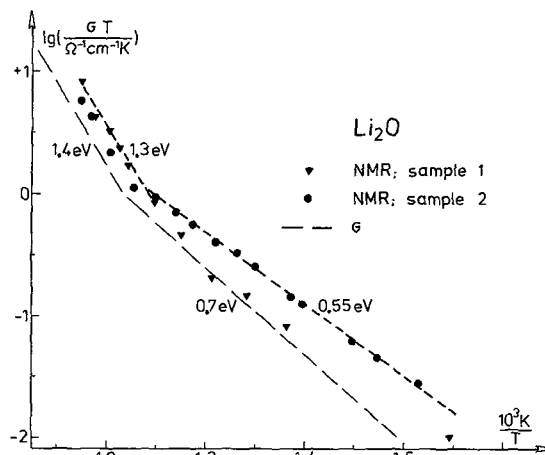

Fig. 2. — Cationic conductivity in Li$_2$O derived from ^{7}Li relaxation rates. — — — : conductivity measured directly.

rent samples (mechanism 1). With sample 1 which contains less concentration of OH$^-$ ions than sample 2, v is larger in the intrinsic region and smaller in the extrinsic region. The level of OH$^-$ impurities in the sample used for the conductivity measurements is not known since it might have been increased during the preparation. Our measured conductivity is somewhat smaller than that obtained from the relaxation rate for mechanism 1. Other simple diffusion mechanisms have larger jump distances and would lead, therefore, to higher calculated values for $\sigma . T$. The conductivity reported by Huggins [10] for the extrinsic region is about 10 times larger than that measured by us. The activation energies obtained from the relaxation rates with the spectral density for mechanism 1 are $\varepsilon_1 = (1.3 \pm 0.1)$ eV for the intrinsic region and $\varepsilon_2 = (0.55 \pm 0.05)$ eV for the diffusion of vacancies.

The spin-lattice relaxation rate for ^{23}Na in Na$_2$S behaves qualitatively similar as observed for ^{7}Li in Li$_2$S and Li$_2$O. The peak rate, however, is about

100 times faster than calculated for dipole interaction and the nuclear magnetisation decays with time in a way which is typical for quadrupolar interaction. The relaxation is therefore attributed to the fluctuating interactions, which originate from the relative diffusion of Na^+ ions (carrying a nuclear quadrupole moment) and atomic defects (which generate an electric field gradient in the cubic Na_2S lattice) [11]. The most important defects in Na_2S are probably S_2^{2-} ions or other foreign anions. Since these defects are immobile as compared with the cations, the correlation time derived from the relaxation rate is given by $(1/\tau) = v.f$. The nmr correlation factor for mechanism 1 is $f = 0.54$ with this type of quadrupole relaxation. Figure 3 shows a comparison of the cationic conductivity calculated from v for mechanism 1 with the directly determined conductivity (our data coincide with those of Möbius et al. [1]).
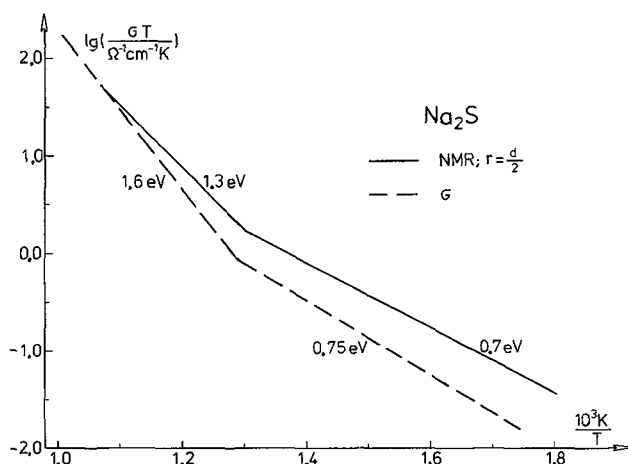

Fig. 3. — Cationic conductivity in Na_2S derived from ^{23}Na relaxation rates. — — — : conductivity measured directly.

For Na_2O, the relaxation rate rises between 250 and 500 °C in a similar manner as for Na_2S between 300 and 500 °C but then remains constant instead of falling off again. From the high values and the rate law of the relaxation it is concluded that quadrupole interactions prevail. Since no maximum is observed, absolute values of jump frequencies cannot be obtained. From the increase in relaxation rate an activation energy of about 0.7 eV is inferred. An independence of relaxation rate on temperature, frequency and addition of foreign substances, similar to that of ^{23}Na in Na_2O above 500 °C is observed for ^{35}Cl in $SrCl_2$ above 700 °C. $SrCl_2$ shows a pronounced anomaly of specific heat between 600 and 800 °C [12].
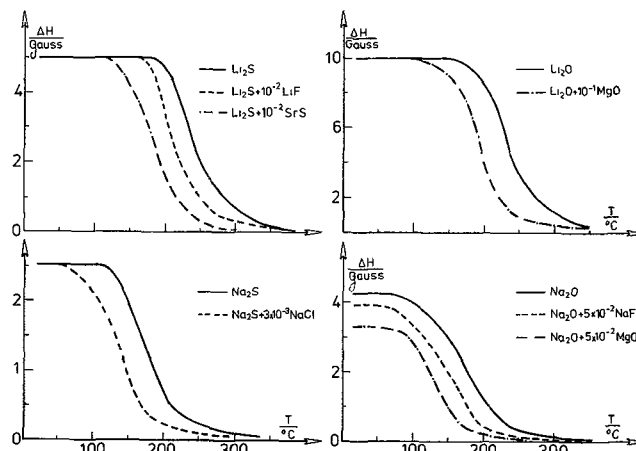

Fig. 4. — Motional narrowing of ^7Li and ^{23}Na nmr linewidths in Li_2S, Li_2O, Na_2S and Na_2O.

It has been reported, that such an anomaly also shows up with Na_2O at about 300 °C [13].

The addition of monovalent anions and of divalent cations to Li_2S, Li_2O, Na_2S and Na_2O enhances the cation jump frequency at low temperatures. This is shown in figure 4 : the motional narrowing of the nmr absorption lines is shifted to lower temperatures under the additions. The high amounts of additives were used in order to get as large an enhancement as possible. The limit of solubility probably in no case exceeds 10^{-2} at 150 °C.

4. **Conclusions.** — For Li_2S, Li_2O and Na_2S jump frequencies of the cations in the intrinsic region could be determined. The apparent activation energies do not exceed 1.5 eV. Diffusion of cations in Na_2S is about 2 times faster than in Li_2S and about 20 times faster than in Li_2O. In the extrinsic region diffusion via cation vacancies prevails with an apparent activation energy not smaller than 0.5 eV. The results for Li_2S and Li_2O are more reliable since dipole interaction predominates. For Li_2O the finding that in sample 2 (containing more vacancies than sample 1) the cation jump frequency is larger at low and smaller at high temperature than in sample 1 indicates Frenkel disorder of the cations.

The comparison of the nmr results with conductivities measured directly excludes a marked anionic contribution to the conduction but does not allow the elucidation of the jump mechanism. It favors, however, a jump process into vacancies on nearest neighbour positions.

For Na_2O the relaxation rates above 500 °C cannot be explained by any simple jump mechanism.

DISCUSSION

Question. — E. E. HELLSTROM.

Several anti-fluorites have been shown to have a high-temperature heat capacity anomally which is

analogous to that seen in the fluorites. In the fluorites, at temperatures just above the temperature at which the heat capacity anomally occurs, the ionic conduc-

tivity levels off as a function of temperature. An analogous levelling off region was not shown in the log (σT) vs. $1/T$ curves for the anti-fluorites, over the temperature range investigated. Do you expect a levelling off in the conductivity at higher temperatures ?

Reply. — H. RICHTERING.

We measured the conductivity up to 700 °C, 780 °C and 850 °C for Li_2S, Na_2S and Li_2O respectively. We did not observe a levelling off in this range. I cannot predict what may happen at higher temperatures. I am not aware of any observation of a specific heat anomally with these substances. For Na_2O, however, such an anomaly has been reported.

Question. — O. KANERT.

1. How have you determined the strength of the quadruple interaction in your ^{23}Na relaxation results ?

2. Is it possible to get more information by $T_{1\rho}$ measurements in the case of the system Na_2O.

Reply. — H. RICHTERING.

1. The peak relaxation rate in Na_2S occurs at 540 °C and is 45 s^{-1} at 15 MHZ. If the field gradients are assumed to be caused by singley charged anions (represented by point charges) the concentration of these defects must be about 2 000 ppm.

2. It should be possible to get cation jump frequencies from $T_{1\rho}$ measurements. These frequencies, however, would probably not extend into the intrinsic region.

References

[1] MÖBIUS, H. H., WITZMANN, H. and HARTUNG, R., *Z. Phys. Chem. Leipzig* **224** (1964) 40.

[2] OEI, Y. S. and RICHTERING, H., *Ber. Bunsenges. Phys. Chem.* **80** (1976) 1007.

[3] PEARSON, T. G. and ROBINSON, P. L., *J. Chem. Soc.* **1931** 4.

[4] COURTOIS, G., *C. R. Hebd. Séan. Acad. Sci.* **207** (1938) 1220.

[5] TORREY, H. C., *Phys. Rev.* **92** (1953) 962.

[6] RESING, H. A. and TORREY, H. C., *Phys. Rev.* **131** (1963) 1102.

[7] SHOLL, C. A., *J. Phys. C. : Solid State Phys.* **7** (1974) 3378, **8** (1975) 1737.

[8] EISENSTADT, M. and REDFIELD, A. G., *Phys. Rev.* **132** (1963) 635.

[9] WOLF, D., FIGUEROA, D. R. and STRANGE, J. H., *Phys. Rev.* **B 15** (1977) 2545.

[10] HUGGINS, R. A., *Electrochimica Acta* **22** (1977) 773.

[11] RICHTERING, H., BECKER, K. D. and HAMANN, H., *J. Physique Colloq.* **34** (1976) C7-373.

[12] DWORKIN, A. S. and BREDIG, M. A., *J. Phys. Chem.* **72** (1968) 1277.

[13] GRIMLEY, R. T. and MARGRAVE, J. L., *J. Phys. Chem.* **64** (1960) 1763.