

Intracrystalline Equilibrium Reaction in a Protonic Conductor

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In quasielastic incoherent neutron scattering studies on the protonic conductor $\text{Rb}_3\text{H}(\text{SeO}_4)_2$, with a dynamic range from 1 μeV to 10 meV, the details of the mechanism of long-range proton diffusion were unraveled. As a result we propose a dynamic disorder in the form of an intracrystalline chemical equilibrium reaction: alternation between the association of the monomers $[\text{HSeO}_4]^{1-}$ and $[\text{SeO}_4]^{2-}$ resulting in the dimer $[\text{H}(\text{SeO}_4)_2]^{3-}$ (H-bond formation) and the dissociation of the latter into the two monomers (H-bond breaking). A 'trigonal asymmetric H-bond' (TAHB) model based on the assumption of time-dependent potentials, agrees well with the measured spectra. In this paper we derive, from an analysis of the measured EISF, the proton-density distribution observed on the 10^{-11} s to 10^{-10} s time-scale, which has lead us to develop this model.

KEYWORDS: neutron scattering, proton conduction, proton diffusion, hydrogen bond, $\text{Rb}_3\text{H}(\text{SeO}_4)_2$

§1. Introduction

High protonic conductivity is intimately related with fast translational charge diffusion. Various basic types of proton conduction mechanisms have been discussed in the literature;¹⁾ the most relevant one for the present study is the Grotthuss mechanism.²⁾ Essentially it consists of a sequence of alternating translational and rotational steps of proton motion. The proton is exchanged via a hydrogen bridge between different molecular subunits. Subsequently, the acceptor molecule transfers the proton into another H-bond by a reorientational motion, whereby the rotating molecule remains on its site. The repeated occurrence of this process gives rise to an uninterrupted trajectory of proton migration and thus to protonic conductivity. A well-known example is the quasi-twodimensional superprotonic conductor phase of $\text{CsOH}\cdot\text{H}_2\text{O}$. It has a trigonal structure consisting of pseudo-hexagonal planar $[\text{H}_2\text{O}\cdot\text{OH}]^-$ networks sandwiched between (and alternating with) Cs^+ -ion layers. Protons are transported through the crystal lattice by a combination of translational motion through the H-bridge connecting adjacent H_2O - and OH^- -groups and reorientation of OH^- -groups, as has been shown previously by quasielastic incoherent neutron scattering (QINS) experiments.³⁾ A similar mechanism has been observed in $\beta\text{-Zr}(\text{HPO}_4)_2$.⁴⁾ In the present paper we report results from QINS-studies on the solid state protonic conductor $\text{Rb}_3\text{H}(\text{SeO}_4)_2$, which have revealed a much more complex mechanism than observed in the above-mentioned examples. After briefly reviewing structural, conductivity and QINS information on $\text{Rb}_3\text{H}(\text{SeO}_4)_2$ in §2, the basis of the "trigonal-asymmetric hydrogen-bond (TAHB)" model will be derived in §3 from a comparison of the measured, (observation-time dependent) EISF with the EISFs calculated for a number of plausible models. Finally, in §4, the results of fitting the TAHB model to the data will

be interpreted in terms of an intracrystalline chemical reaction equilibrium, and some numerical values of the model parameters will be given.

§2. Structure, Protonic Conductivity and Proton Diffusion in $\text{Rb}_3\text{H}(\text{SeO}_4)_2$

$\text{Rb}_3\text{H}(\text{SeO}_4)_2$ is a member of a class of (essentially) isostructural compounds with the general formula $\text{M}_3\text{H}(\text{AO}_4)_2$, exhibiting high-temperature modifications with high protonic conductivity, where $\text{A}=\text{S}$ or Se and where the M position is occupied by an alkali metal ion (Na^+ , K^+ , Cs^+ or Rb^+) or by the ammonium group $(\text{NH}_4)^+$. The crystal structure can be described as a sequence of $\text{Rb}\cdot\cdot\text{H}[\text{SeO}_4]_2$ -layers alternating with Rb-coordination polyhedra layers, both perpendicular to the pseudo-hexagonal c-axis. The rubidium atoms in the Rb-layers, of type Rb(2), have 9-fold coordination by the oxygen atoms forming the bases (O(1), O(3) and O(4)) of the selenate tetrahedra, which are parallel to the layers. The top oxygen atoms (O(2)) of the selenate tetrahedra are connected by hydrogen bonds with each-other, forming $[\text{H}(\text{SeO}_4)_2]^{3-}$ dimers at low temperatures ("zero-dimensional" H-bond network) and layers of two-dimensional dynamically disordered H-bond networks in the proton conducting high-temperature phase ($T > 449$ K). The time averaged structure of this phase is trigonal ($R\bar{3}m$), whereas the low-temperature structure is monoclinic ($C2/c$).⁵⁻⁸⁾ The phase transition shows lattice parameter discontinuities typical for first-order transitions and the protonic conductivity σ in the H^+ -conducting layers increases by two orders of magnitude up to about $3 \times 10^{-3} \text{ Scm}^{-1}$ within a few degrees near the transition temperature, whereas at room temperature it is of the order of 10^{-9} Scm^{-1} .⁹⁾ Using the Nernst-Einstein equation, which connects the ionic conductivity, the number density of charge carriers and the coefficient of self-diffusion, one sees immediately, that QINS experiments should be able to reveal details of the proton diffu-

sion mechanism. We have carried out such experiments at three different temperatures with the high-resolution time-of-flight spectrometer NEAT at BENS and with the backscattering spectrometer IN10 at ILL, using 4 different energy resolutions. Here we will only present results from the lowest resolution measurements, while a full report on all measurements is deferred to a later publication. A comparison of the measured spectra with the simplest models, such as translational diffusion alone (Chudley-Elliott model), localized jump diffusion on two or three equivalent sites, and combinations of these models with each other, did not lead to an adequate description of the measured spectra. This is demonstrated in Fig. 1, where values of a phenomenologically determined "apparent" EISF and calculated curves of the theoretical EISF^{10,11} for a few examples of such models are shown. Here, a range of jump distances has been tested, which would at first sight appear plausible in view of the time-averaged structure as obtained from crystallographic studies. In analogy to the cases discussed in refs.^{3,4} 2-site jumps would correspond to proton motion within the hydrogen bridge and 3-site jumps to "OH"-reorientation of protons around the top-oxygens of selenate tetrahedra. It is quite evident from the figure, that the calculated curves deviate in such a way from the measured behaviour of the EISF, that agreement can not be obtained for any value of the jump distances in the framework of these simple models. A qualitative inspection of the EISF data and the discrepancy with these models suggests, that an EISF based on a proton-density distributed over a set of non-equivalent sites comprising more than one H-bond is required. A successful model implying non-equivalent sites due to asymmetric double-well potentials will be presented in the following.

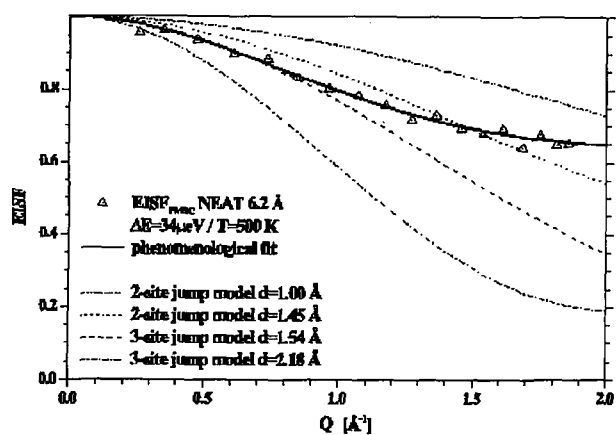


Fig.1. Comparison of phenomenologically determined "apparent" EISF (from time-of-flight experiment; resolution FWHM=34 μ eV) with theoretical curves for several plausible proton jump models. The solid curve is a purely phenomenological function fitted to the experimental points(triangles).

§3. EISF Models for The Localized Diffusive Proton Motion

Since the fast localized diffusive motion can not be described by simple models of motion restricted to the limited space of intra-H-bond or inter-H-bond jumps alone, it is likely that the proton-density distribution resulting from this motion on a time-scale of the order of 10^{-11} s to 10^{-10} s (energy resolution, FWHM : 34 μ eV; observation time: $\approx 0.4 \times 10^{-10}$ s) already has the time-averaged trigonal symmetry of the lattice. Therefore we assume, that this distribution comprises the regions of the three H-bonds connecting a given (selenate top) oxygen to its three neighbouring selenate top oxygens in the same proton conducting plane. In other words: a proton is assumed to explore the quasi-twodimensional space around an oxygen atom for some time, before it crosses a hydrogen bridge, in order to definitely join another oxygen atom. Let us now consider a number of such local site arrangements, which might be compatible with the trigonal structure of $\text{Rb}_3\text{H}(\text{SeO}_4)_2$. The general expression for the single-crystal EISF of an ensemble comprising a finite number N of inequivalent sites is given by:¹¹

$$A_0(Q) = \sum_{j=1}^N a_j e^{i\mathbf{Q} \cdot \mathbf{R}_j} \cdot \sum_{i=1}^N a_i e^{-i\mathbf{Q} \cdot \mathbf{R}_i},$$

$$= \sum_{j=1}^N \sum_{i=1}^N a_j a_i e^{i\mathbf{Q} \cdot \mathbf{R}_{ji}}, \quad (3.1)$$

where \mathbf{Q} is the momentum transfer vector, $\mathbf{R}_{ji} = \mathbf{R}_j - \mathbf{R}_i$ is the difference vector between the sites j and i, a_j and a_i are the occupation probabilities of these proton sites. The orientational average required in the case of a polycrystalline sample, reads:

$$A_0(Q) = \sum_{j=1}^N \sum_{i=1}^N a_j a_i j_0(Q R_{ji}), \quad (3.2)$$

where j_0 is the zero order spherical Bessel function. We have tested the EISF of the site arrangement shown in

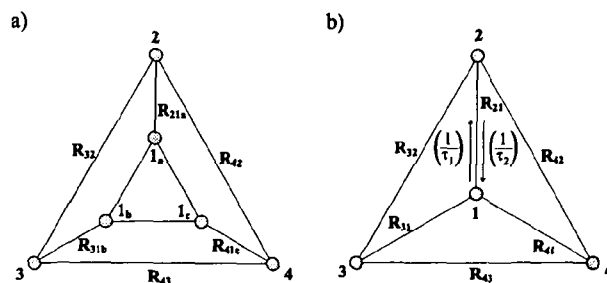


Fig.2. Trigonal asymmetric H-bond (TAHB) model: a) the 3 vectors \mathbf{R}_{21a} , \mathbf{R}_{31b} and \mathbf{R}_{41c} connecting proton sites, represent the 3 H-bridges centered around an oxygen site in the proton conducting plane of $\text{Rb}_3\text{H}(\text{SeO}_4)_2$. The occupation probabilities of the 3 inner sites generally differ from those of the outer sites. b) special case of a), where the three inner sites have "collapsed" to one single site 1 (see text)

Fig. 2a against the data of Fig. 1. This group of 6 sites ($N = 6$) has trigonal symmetry and consists of three outer and three inner proton sites, with equal occupation probabilities for the three sites (a_{1a} , a_{1b} , a_{1c} and a_2 , a_3 , a_4 , respectively) on each of the two triangles. The occupancies of the inner triangle are allowed to be different from the outer ones. The site pairs, (1_a, 2), (1_b, 3) and (1_c, 4), correspond to the three H-bonds. A fit of the corresponding EISF to the data, with 3 free parameters, namely one of the occupation probabilities (the others being not independent because of particle conservation) and the sizes of the two triangles (represented by the distances of the sites from the origin in the center of the triangles), firstly lead to a "collapse" of the inner triangle into one single point: the site 1 in Fig. 2b, which is also the average location of the selenate top oxygen (in a projection along the *c*-axis). Secondly, the sum of the inner occupancies turned out to be at least 5 times larger than the sum of the outer occupation probabilities. This indicates an appreciable asymmetry of the potential in which the proton is moving in each hydrogen bridge on the time-scale of this experiment. This observation was the starting point for the development of the TAHB model, which will be discussed briefly in the next paragraph. We note, that the observed collapse is only a virtual one. Measurements on a much shorter time scale (energy resolution $\Delta E = 300 \mu\text{eV}$) suggest the existence of a fast motion of the proton around the oxygen, which is not seen on the longer time scales (due to the problem of signal to noise ratio at higher energy transfers, systematically present in high-resolution measurements) and hence not taken into account in the phenomenological determination of the apparent EISF. This does however not invalidate the results of the high-resolution experiment.

§4. TAHB Model, Intracrystalline Chemical Equilibrium Reaction and Conclusion

The trigonal-asymmetric hydrogen bond model can be described using Fig. 2b: The central site 1, with the average proton residence time τ_1 , is connected to the 3 external sites, with residence times τ_2 , by the jump vectors \mathbf{R}_{21} , \mathbf{R}_{31} and \mathbf{R}_{41} . The jump rates are $1/\tau_1$ and $1/\tau_2$ for proton jumps to the external sites and to the internal site, respectively. It is assumed, that no direct jumps are taking place between the sites 2, 3 and 4. The solution of the system of rate equations describing this situation will be given in a subsequent paper.¹²⁾ The neutron scattering function derived from this solution was fitted to the QINS spectra mentioned in §2, and proton residence

times, as well as activation energies were obtained. Due to limited space only a few essential results can be given here.

In the temperature range from 460 K to 500 K, τ_1 varies from 15.2×10^{-10} s to 8.9×10^{-10} s, τ_2 from 0.62×10^{-10} s to 0.43×10^{-10} s. The corresponding activation energies are 3080 K and 2140 K, respectively, the asymmetry of the potential is 940 K. We interpret these observations as the consequence of a dynamic disorder in the form of an intracrystalline chemical equilibrium reaction: alternation between the association of the monomers $[\text{HSeO}_4]^{1-}$ and $[\text{SeO}_4]^{2-}$, resulting in the dimer $[\text{H}(\text{SeO}_4)_2]^{3-}$ (H-bond formation) and the dissociation of the latter into the two monomers (H-bond breaking). This picture has been confirmed by a spectroscopic investigation carried out in parallel using incoherent inelastic neutron scattering (IINS) and Fourier transform infrared (FTIR) techniques, in which specific vibrational modes of the $[\text{SeO}_4]^{2-}$ and the $[\text{HSeO}_4]^{1-}$ groups have been identified and a drastic increase of their intensities has been observed upon approaching and crossing the transition temperature towards the solid-state protonic conductor phase. A full account of all these results will be presented in a later paper.¹³⁾

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- 1) R. E. Lechner: *Ferroelectrics* **167** (1995) 83.
- 2) C. J. T. von Groththuss: *Ann. Chim.* **LVIII** (1806) 54.
- 3) R. E. Lechner, T. Dippel, R. Marx and I. Lamprecht: *Solid State Ionics* **61** (1993) 47.
- 4) R. E. Lechner, R. Melzer and J. Fitter: *Physica B* **226** (1996) 86.
- 5) I. P. Makarova, I. A. Verin and N. M. Shchagina: *Sov. Phys. Crystallogr.* **31** (1986) 105.
- 6) A. Bohn, R. Melzer, R. Sonntag, R. E. Lechner, G. Schuck and K. Langer: *Solid State Ionics* **77** (1995) 111.
- 7) R. Melzer, R. Sonntag and K. S. Knight: *Acta. Cryst. C* **52** (1996) 1061.
- 8) R. Melzer, T. Wessels and M. Reehuis: *Solid State Ionics* **92** (1996) 119.
- 9) A. Pawlowski and C. Pawlaczyk: *Ferroelectrics* **81** (1988) 201.
- 10) A. J. Leadbetter and R. E. Lechner: *The Plastically Crystalline State*, ed. J. N. Sherwood (J. Wiley & Sons, New York 1979) p. 285.
- 11) R. E. Lechner: *Quasielastic Neutron Scattering*, San Sebastian, 1993, eds. J. Colmenero *et al.* (World Scientific Singapore 1994) p. 62.
- 12) R. E. Lechner: to be published.
- 13) G. Schuck, R. E. Lechner and K. Langer: to be published.