# Interrelationship between Number of Mobile Protons, Diffusion Coefficient, and AC Conductivity in Superprotonic Conductors, CsHSO<sub>4</sub> and Rb<sub>3</sub>H(SeO<sub>4</sub>)<sub>2</sub>

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Using quasielastic neutron scattering (QENS), we investigated the proton dynamics for two superprotonic conductors, CsHSO<sub>4</sub> and Rb<sub>3</sub>H(SeO<sub>4</sub>)<sub>2</sub>. To evaluate the self-diffusion coefficients and the number of mobile protons on both superprotonic and normal phases, we focused on proton dynamics not only in the phase above  $T_c$ , but also in the phase below  $T_c$ . In Rb<sub>3</sub>H(SeO<sub>4</sub>)<sub>2</sub>, the self-diffusion of protons was observed even below the  $T_c$  phase. In contrast to popular belief, no large changes in the self-diffusion coefficients were observed across  $T_c$ . Nevertheless, the increase in the number of mobile protons across  $T_c$  was about 14.5 times, which was estimated from the integrated intensity of QENS spectra, and this change could not account for the increased magnitude of proton conductivity, which is about 500 times. As a large translational self-diffusion coefficient has not been reported in previous works by QENS experiments, there are still unknown factors that contribute to the Nernst–Einstein relation that need to be discovered.

## 1. Introduction

Ferroelastic and/or ferroelectric materials containing protons sometimes exhibit a huge jump in AC conductivity ( $\sigma$ ), such as 4–8 orders of magnitude, accompanied by a structural phase transition at  $T_c$ .<sup>1,2)</sup> The mechanism for the marked increase in  $\sigma$  at  $T_c$  relates to the appearance of an extremely large proton conductivity. Therefore, such materials are often called as "superprotonic conducting (SPC)" materials. Due to the large proton conductivity, superprotonic conductors are considered to be a class of promising application materials for electrolytes of fuel cells. Their proton conductivity, however, is still two orders lower than that required for practical applications. Therefore, clarifying the SPC mechanism is important not only for the scientific community but also for practical applications to determine if there is room for increasing the conductivity.

To study the basic mechanism of SPC, Belusikin and coworkers<sup>3,4)</sup> carried out a pioneering investigation using quasielastic neutron scattering (QENS) for several SPC materials. In particular, for the SPC phase in CsHSO<sub>4</sub>, they reported the presence of two different types of proton motion namely, the rotational mode of protons due to the rotation of the  $SO_4^{2-}$  anion group and the slower long-range translational self-diffusion mode. They concluded that the latter is responsible for the SPC mechanism. The extended model of the proton migration mechanism that relates to the rotational motion of the  $\text{SeO}_4^{2-}$  group in  $\text{Rb}_3\text{H}(\text{SeO}_4)_2$  has also been proposed by other researchers.<sup>5,6)</sup> On the other hand, the partial decomposition of H<sub>2</sub>O was proposed to play a significant role in the appearance of SPC, based on differential scanning calorimetry (DSC) and conductivity measurements.<sup>7)</sup> Recently, a "considerable" increase in the number of mobile protons across the superprotonic structural phase transition has been explained in terms of an increase in the number of sites to which the protons can jump.<sup>8)</sup> Although a consensus of the driving force of protons in the SPC phase is obtained as a faster rotational motion of  $SO_4^{2-}$ , the transport mechanism (proton dynamics) that contributes directly to a marked AC conductivity has not yet been clarified.

Owing to the ability of QENS, proton dynamics, such as the number of mobile protons (n) and the diffusion coefficient (D), can be connected with the degree of proton conductivity  $\sigma_n (\propto n \cdot D)$  according to the Nernst-Einstein relation. The Nernst-Einstein relation is an elementary expression that connects the diffusion coefficient and mobility in liquid. It is also frequently used for the evaluation of the diffusion coefficient using extended formulas in solid.<sup>9)</sup> However, the diffusion coefficient evaluated from direct observation techniques, e.g., quasi-elastic neutron scattering,  $\mu$ SR, and the tracer method, and the estimated diffusion coefficient by AC conductivity through the Nernst-Einstein relation sometimes show a large difference with an exponential order. Until now, research studies of proton dynamics have been carried out only for the superprotonic conducting phase, but not for the normal phase. Therefore, to investigate this marked transport phenomenon, it is necessary to investigate proton dynamics (self-diffusion coefficient and number of mobile protons) not only in the superprotonic phase but also in the low-temperature normal phase.

It is important to note that SPC materials are categorized into two classes.<sup>2)</sup> Some SPC materials show a small  $\sigma$  below  $T_{\rm c}$ , but an extremely large  $\sigma$  above  $T_{\rm c}$ . A typical material for this class is CsHSO<sub>4</sub>.<sup>10)</sup> For materials belonging to the second class,  $\sigma$  increases exponentially with increasing T even below  $T_{\rm c}$ , followed by an abrupt increase in  $\sigma$  at  $T_{\rm c}$ . Rb<sub>3</sub>H(SeO<sub>4</sub>)<sub>2</sub> belongs to the second class.<sup>11</sup> We naturally need a common mechanism to explain SPC materials for both classes. It is expected that a thorough comparison of proton dynamics below and above  $T_c$  will shed some light on the origin of SPC. In addition, by comparing materials for both classes, we can clarify the reason why  $\sigma$  in the class of superprotonic materials  $Rb_3H(SeO_4)_2$  systematically increases with T even below  $T_{\rm c}$ . Since it has a relatively large  $\sigma$  even below  $T_{\rm c}$ , we have a good chance of detecting the self-diffusion of protons in the normal phase using a backscattering spectrometer with a high energy-resolution, i.e.,  $d\omega \sim 1 \,\mu\text{eV}$ . Here, we present the proton dynamics for both  $Rb_3H(SeO_4)_2$  and  $CsHSO_4$  in the wide *T* range so as to cover the temperatures below and above  $T_c$ .

#### 2. Experimental Details

Powder samples of Rb<sub>3</sub>H(SeO<sub>4</sub>)<sub>2</sub> and CsHSO<sub>4</sub> were prepared by crushing single crystals of Rb<sub>3</sub>H(SeO<sub>4</sub>)<sub>2</sub> and CsHSO<sub>4</sub>. Details of the crystal growth are described elsewhere.<sup>10,11</sup> The samples were handled carefully to avoid exposure to moisture, and they were kept in vacuum at room temperature until the measurements. Neutron measurements were carried out at the High Flux Back scattering Spectrometer<sup>12)</sup> (HFBS) located at the NIST Center for Neutron Research in the U.S. Although the wave-length of incident neutron is 6.271 Å the energy resolution is  $\sim 1 \,\mu eV$  due to back scattering geometry. In the HFBS measurements, the sample temperatures were kept below the decomposition temperature of the compounds. Both multiple scattering<sup>13)</sup> and absorption were negligible in the QENS measurements, because thin samples were loaded into the gap of double cylindrical shape sample holder made of aluminum (high transmission). In addition, except temperature change in the vicinity of  $T_{\rm c}$ , any experimental conditions were not changed, that is both the background and absorption effects must not be changed. The neutron data were packed, analyzed, and/or visualized using the computer program DAVE.<sup>14)</sup>

#### 3. Results and Discussion

Figure 1 shows the temperature (*T*) dependences of AC conductivity  $\sigma$  and normalized mean-square displacement (MSD) for Rb<sub>3</sub>H(SeO<sub>4</sub>)<sub>2</sub> and CsHSO<sub>4</sub>. The normalized MSD is defined as  $\delta \langle u^2 \rangle \equiv \langle u^2 \rangle (T) - \langle u^2 \rangle (T \rightarrow 4 \text{ K})$ , which was obtained from the elastic intensity I(Q, 0) of energy spectra. I(Q, 0) was measured using the fixed window scan data for Rb<sub>3</sub>H(SeO<sub>4</sub>)<sub>2</sub> and CsHSO<sub>4</sub>. All elastic neutrons were counted as a function of *T* in the Doppler stopped mode of HFBS. The neutron scattering intensity  $I(Q, \omega)$  is expressed with a convolution of the neutron scattering function  $S(Q, \omega)$  and the resolution function  $R(Q, \omega)$  as

$$I(Q,\omega) = \int_{-\infty}^{\infty} S_{\rm inc}(Q,\omega') R(Q,\omega-\omega') \, d\omega'.$$
(1)

The wave vector dependence of elastically scattered intensity I(Q, 0) at each temperature can be utilized to extract MSD according to

$$I(Q,0) = I(0,0) \cdot \exp(-\langle u^2 \rangle Q^2).$$
<sup>(2)</sup>

In Eq. (2),  $\langle u^2 \rangle$  denotes the MSD of (hydrogen) atoms within the sample. An abrupt change in MSD is clearly seen for both Rb<sub>3</sub>H(SeO<sub>4</sub>)<sub>2</sub> and CsHSO<sub>4</sub> at  $T_c$ , at which the  $\sigma(T)$  curve also exhibits an apparent jump. Since the slope  $(d\delta \langle u^2 \rangle / dT)$ changes at  $T_c$ , the lattice vibration above  $T_c$  deviates from Debye's approximation, which is naturally ascribed to the diffusion of protons with a large incoherent neutron scattering cross section.

The representative energy spectra at  $Q = 0.74 \text{ Å}^{-1}$  below  $T_c$  for both Rb<sub>3</sub>H(SeO<sub>4</sub>)<sub>2</sub> ( $T = 440 \text{ K} < T_c$ ) and CsHSO<sub>4</sub> ( $T = 400 \text{ K} < T_c$ ) are shown in Figs. 2(a) and 2(b), respectively. The instrumental resolutions are used from the spectra observed at 30 K for Rb<sub>3</sub>H(SeO<sub>4</sub>)<sub>2</sub> and at 4 K for CsHSO<sub>4</sub>. At  $T < T_c$ , we can clearly see a quasielastic scattering broad-



**Fig. 1.** AC conductivities  $\sigma$  for (a) Rb<sub>3</sub>H(SeO<sub>4</sub>)<sub>2</sub> (10 K Hz)<sup>11</sup> and (b) CsHSO<sub>4</sub> (1 M Hz).<sup>10</sup> *T* dependences of MSD for (c) Rb<sub>3</sub>H(SeO<sub>4</sub>)<sub>2</sub> and (d) CsHSO<sub>4</sub>.



**Fig. 2.** (Color online) Energy spectra at  $Q = 0.74 \text{ Å}^{-1}$ , representatively, for Rb<sub>3</sub>H(SeO<sub>4</sub>)<sub>2</sub> T = 440 K ( $< T_c$ ) (a), T = 510 K ( $> T_c$ ) (c), and for CsHSO<sub>4</sub> T = 400 K ( $< T_c$ ) (b), T = 463 K ( $> T_c$ ) (d). Error bars throughout this paper represent one standard deviation.

ening in the Rb<sub>3</sub>H(SeO<sub>4</sub>)<sub>2</sub> spectrum, which is well fitted by the combination of a background (BG), a delta function  $\delta(\omega)$ , and a Lorentzian, after convoluting them with the instrumental resolution [see Fig. 2(a)]. On the other hand, the shape of the spectrum for CsHSO<sub>4</sub> is almost identical to the instrumental resolution [see Fig. 2(b)], indicating that the proton motion is static below  $T_c$  for CsHSO<sub>4</sub> within the energy resolution of this spectrometer ( $\sim 1 \,\mu eV$ ). It is interesting to note that quasielastic scattering broadening was observed only above  $T_c$  for CsHSO<sub>4</sub>, while both below and above  $T_c$  for Rb<sub>3</sub>H(SeO<sub>4</sub>)<sub>2</sub>. On the basis of DSC measurements,<sup>5)</sup> the origin of SPC for CsHSO<sub>4</sub> was proposed as proton diffusion assisted by water that was generated during partial decomposition above 395 K. However, we did not observe any changes in the measured MSD and no detectable QENS signal at 400 K ( $< T_c$ ) for CsHSO<sub>4</sub>; such diffusion is unlikely for SPC. Here, we would like to emphasize that neutrons are very sensitive to hydrogen (H)<sup>15)</sup> and time scales of water dynamics suit perfectly the backscattering time window. The energy spectrum changes markedly at T above  $T_c$  for both samples [see Figs. 2(c) and 2(d)]. The two spectra are fitted by the combination of a flat



**Fig. 3.** (Color online) FWHM versus Q curve for Rb<sub>3</sub>H(SeO<sub>4</sub>)<sub>2</sub> at (a) T = 440 K ( $< T_c$ ) and at T = 460 K ( $> T_c$ ) of wide (b) and narrow (c) components. (d) Schematic overview of existing component for Rb<sub>3</sub>H-(SeO<sub>4</sub>)<sub>2</sub> and CsHSO<sub>4</sub> below and above  $T_c$ . FWHM versus Q curve for CsHSO<sub>4</sub> at T = 463 K ( $> T_c$ ) of wide (e) and narrow (f) components. The solid line represents the fitting result using a jump diffusion model. Note that we omitted plot data at some Q position intentionally owing to the Bragg peak position and very large deviation/error positions.

background (BG), a delta function, and two Lorentzians, after convoluting them with the instrumental resolution.

The full width at half maximum (FWHM) of the single Lorentzian  $\Gamma_{\rm FWHM}$  for Rb<sub>3</sub>H(SeO<sub>4</sub>)<sub>2</sub> below  $T_{\rm c}$  is displayed as a function of Q in Fig. 3(a). The  $\Gamma_{\rm FWHM}(Q)$  curves for the two Lorentzians (wide and narrow components) for Rb<sub>3</sub>H(SeO<sub>4</sub>)<sub>2</sub> and CsHSO<sub>4</sub> above  $T_{\rm c}$  are also shown in Figs. 3(b)–3(f). FWHM of the two components decrease towards 0 by  $Q \rightarrow 0$ , although the data including error bar in low Q is too large ambiguity to divide two spectra and is omitted. Therefore, it is appropriate to use the jump diffusion model set for  $\Gamma_{\rm FWHM}(Q) \rightarrow 0$  as  $Q \rightarrow 0$ . Each  $\Gamma_{\rm FWHM}(Q)$ curve is fitted by the following jump diffusion model<sup>16,17)</sup>

$$\Gamma_{\rm FWHM}(Q) = \left(\frac{1}{\tau}\right) \left\{ \frac{1 - \sin(Q\ell)}{Q\ell} \right\},\tag{3}$$

where  $\tau$  is the residence time and  $\ell$  is the diffusion length.

The obtained  $\ell$  and  $\tau$  are shown in Table I. The nearestneighbor proton sites in the  $T > T_c$  phase of Rb<sub>3</sub>H(SeO<sub>4</sub>)<sub>2</sub> and CsHSO<sub>4</sub> are about 3 Å, but are about 7 and 4 Å in the *c*-axis direction, respectively. If we look at the results of CsHSO<sub>4</sub> alone, it is clear that the proton diffusion length is related to the SPC mechanism. However, when we try to rationalize the results obtained for both materials, then such a simple solution does not seem to work. Comparing the residence times of broad components to that of narrow ones in Rb<sub>3</sub>H(SeO<sub>4</sub>)<sub>2</sub>, it is clear that the latter component has residence times almost one order higher than those of the former. As the average jump length is defined by the diffusion coefficients and also by the residence time, these quantities play an important role in determining the apparent

 Table I. Diffusion length and residence time for superprotonic conductors.

 Rb<sub>1</sub>H(SeO<sub>4</sub>)<sub>2</sub>

	Temperature	Wide		Narrow	
	(K)	ℓ (Å)	$\tau$ (ns)	ℓ (Å)	$\tau$ (ns)
	375	3.84	1.38		
	400	4.34	1.04		
$T < T_{\rm c}$	440	3.84	0.876		
$T > T_{\rm c}$	460	5.34	1.89	4.21	17.4
	475	5.31	1.84		
	490	4.66	1.71	4.57	15.30
	510	4.90	1.50	3.77	9.96
CsHSO <sub>4</sub>					
	Temperature	Wide		Narrow	
	(K)	ℓ (Å)	$\tau$ (ns)	ℓ (Å)	$\tau$ (ns)
$T > T_{\rm c}$	426	6.91	1.71	3.91	11.85
	440	6.83	1.63	4.23	9.96
	463	6.49	1.58	4.39	7.90

jump lengths deduced. There might, however, still be other factors that affect our data and interpretation, and it is not so obvious to correlate the proton conductivity to either the diffusion coefficient or the residence time.

From the obtained  $\ell$  and  $\tau$ , *D* is estimated as

$$D = \frac{\ell^2}{2N \cdot \tau},\tag{4}$$

where *N* is the diffusion dimension of the system.<sup>18)</sup> Note that the energy transfers for the rotational mode<sup>3)</sup> of CsHSO<sub>4</sub> are too large to be visible on HFBS and appear as a flat background. Interestingly, we can see a marked change in the translational self-diffusion mode across  $T_c$  while the background seems to be unchanged, which clearly indicates a clear correspondence of the self-diffusion with the superprotonic conductivity. Thus,  $\sigma$  of Rb<sub>3</sub>H(SeO<sub>4</sub>)<sub>2</sub> below  $T_c$  is considered to be attributed to the translational self-diffusion of protons with  $D \sim 1.2 \times 10^{-8}$  cm<sup>2</sup>/s. This is comparable to  $D_{\text{Large}}$  of the SPC phase of Rb<sub>3</sub>H(SeO<sub>4</sub>)<sub>2</sub>. The characteristic  $\Gamma_{\text{FWHM}}$  of the wide component is almost the same as that of the translational self-diffusion found by Belushkin et al.<sup>3</sup>) Therefore, the wide component is considered to correspond to the translational self-diffusion.

Figure 4 shows the activation energies, which are deduced from the T dependence of logarithm D, of the two superprotonic conductors. Since the broad QENS spectrum above  $T_{\rm c}$  can be split into two Lorentzian components, there are two diffusion coefficients D ( $D_{Large}$  and  $D_{Small}$ ) above  $T_{c}$ for both Rb<sub>3</sub>H(SeO<sub>4</sub>)<sub>2</sub> and CsHSO<sub>4</sub>. Furthermore, the two components are identified as the translational self-diffusion of protons, in accordance with the results of fitting by Eq. (3). However, a new diffusional component is present in  $Rb_3H(SeO_4)_2$  below  $T_c$  unlike CsHSO<sub>4</sub>, which only shows common two processes above  $T_c$ . Therefore, it may be considered that the translational self-diffusion with  $D_{\text{Small}}$ plays an important role in the SPC mechanism. A strong two-dimensional diffusive nature has been observed from our recent QENS result of Rb<sub>3</sub>H(SeO<sub>4</sub>)<sub>2</sub> single crystals. On the basis of this nature, these two diffusion coefficients seem to be attributed to the direction dependences of diffusion coefficients. However, note that there is no marked change in the total width of Lorentzian components. Therefore, we



Fig. 4. (Color online) Temperature dependence of logarithm diffusion coefficients D is plotted for both Rb<sub>3</sub>H(SeO<sub>4</sub>)<sub>2</sub> and CsHSO<sub>4</sub>. Also, calculated activation energies are shown.

verify if the difference in the number of mobile protons across  $T_c$  plays an important role as well, next.

To further the above difference verify, the integrated intensity of the quasielastic components in the spectra and the integrated intensity of the elastic component in the spectra were compared both above and below  $T_c$ . The number of mobile protons corresponds to the integrated intensity of the quasielastic component(s), which can be estimated from fitting functions of the spectra. The integrated intensity  $A_{\text{QENS}}$ of the Lorentzian  $L(\omega)$ , corresponding to the self-diffusion mode, is given by

$$L(\omega) = \frac{B}{\omega^2 + \Gamma^2},$$
(5)

$$A_{\text{QENS}} = \int_{-\infty}^{\infty} L(\omega) \, d\omega = \frac{B\pi}{\Gamma}.$$
 (6)

Here, *B* is the area and  $\Gamma$  is the full width at half maximum of the function. Also, for the elastic component, the integrated intensity  $A_{\text{EL}}$  of the convoluted delta function  $\delta(\omega)$  with the instrumental resolution function  $R(Q, \omega)$  is given as  $G(\omega)$ :

$$G(\omega) = \delta(\omega) \otimes R(Q, \omega), \tag{7}$$

and  $A_{\rm EL}$  is given as

$$A_{\rm EL} = \int_{-\infty}^{\infty} G(\omega) \, d\omega \cong \frac{C}{\xi} \sqrt{\pi}.$$
 (8)

Here, *C* is the peak value and  $\xi$  is the width parameter. The sum of the integrated intensity for Lorentzians increases ~14.5 times above  $T_c$ .<sup>19)</sup> This corresponds to the increase in the number of mobile protons.<sup>20)</sup> Here, as can be seen in Fig. 1, the increased AC conductivity within the measured temperature range of the spectra is about 500 times. According to the Nernst–Einstein relation, the proton conductivity  $\sigma_n$  is given as the number of diffusion ions (*n*) multiplied by the diffusion coefficient (*D*), that is,  $\sigma_n \propto n \cdot D$ .

In contrast to common belief, however, the variation in the integrated intensity at  $T_{\rm c}$  of the quasielastic component does not account for the change in the proton conductivity at  $T_c$ . The ratio of AC conductivity  $\sigma_{(T=510\text{K}>T_c)}/\sigma_{(T=440\text{K}<T_c)}$  and the ratio of  $\sigma_{n(T=510\text{K}>T_c)}/\sigma_{n(T=440\text{K}<T_c)}$  obtained from the diffusion coefficient (D) and proton mobility (n) by neutron measurements through the Nernst-Einstein relation differ by a factor of 35. The difference of more than one order suggests that we might still be missing yet another self-diffusion of protons. Nevertheless, a large translational self-diffusion coefficient has not been reported in previous works by QENS experiments. Therefore, our findings suggest crucial and missing factors in the Nernst-Einstein relation when these calculations are being made, for example, the increase in the number of equivalent vacancy proton sites to which protons can jump, as in the case of the geometrical frustration in Pauling's ice rule.<sup>21,22)</sup>

# 4. Conclusions

In summary, we investigated the proton dynamics of  $Rb_3H(SeO_4)_2$  and  $CsHSO_4$  above and below  $T_c$  using QENS. We have successfully observed the proton dynamics even below  $T_c$  for  $Rb_3H(SeO_4)_2$ . By direct comparison of the variation in the AC conductivity, the self-diffusion coefficient, and the number of mobile protons of  $Rb_3H(SeO_4)_2$  in the vicinity of  $T_c$ , we evaluated the Nernst–Einstein relation directly for these SPC phases. We found an increase in the number of mobile protons across  $T_c$ , which is not sufficient to account for the observed increase in the proton conductivity. This needs to be further investigated probably by other neutron scattering techniques.

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- 18) Our recent QENS measurement for  $Rb_3H(SeO_4)_2$  single crystal suggests N = 2. However, we used N = 3 in this article as details of calculations are still unknown. In addition, this factor alone still cannot account for the missing factors.

- 19) A typical Q of 0.74 Å<sup>-1</sup> was used. The integrated intensity (A) of the Lorentzian below and above  $T_c$  is given as  $A_{\text{Total}(T=440K < T_c)} = A_{\text{EL}(T=440K < T_c)} + A_{\text{QENS}(T=440K < T_c)} \equiv A_{\text{Total}(T=510K > T_c)} + A_{\text{QENS},\text{wide}(T=510K > T_c)} + A_{\text{QENS},\text{marrow}(T=510K > T_c)}$ . Here, integrated intensity (A) is proportional to the number of mobile protons (n) as  $n_{(T=440K < T_c)} \propto A_{\text{QENS},\text{marrow}(T=510K > T_c)}$  and  $n_{(T=510K > T_c)} \propto A_{\text{EL},\text{wide}(T=510K > T_c)} + A_{\text{QENS},\text{marrow}(T=510K > T_c)}$ . Therefore, the ratio of the product of the number of mobile protons (n) and the diffusion coefficient (D) below  $T_c$  to that above  $T_c$  obtained by the neutron result is  $n_{(T=510K > T_c)} \cdot D_{(T=510K > T_c)} / n_{(T=440K < T_c)} \propto \sigma_{n(T=510K > T_c)} / \sigma_{n(T=440K < T_c)} \approx 14.5$ . On the other hand, the ratio of the AC conductivity below to that above  $T_c$  becomes  $\sigma_{(T=510K > T_c)} / \sigma_{(T=440K < T_c)} \approx 500$ .
- 20) Although the absolute number of protons cannot be obtained, the percentage of mobile protons can be evaluated as 5.6% at  $T < T_c$  and as 81% at  $T > T_c$ . Here, the maximum error is estimated to be below 2.4%.
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