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Proton conductivity and spontaneous strain below superprotonic phase transition in $Rb_3H(SeO_4)_2$

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Abstract

We have carried out the ^{1}H-NMR and X-ray measurements, in order to reveal the origin of the relatively high electrical conductivity observed even below a superprotonic phase transition at T_c (=449 K) in $Rb_3H(SeO_4)_2$. It is found that the second moment of the ^{1}H-NMR absorption line rapidly decreases around 338 K with increasing temperature. This result indicates that the hopping motion of a proton, which is the precursor motion of proton motion in the superprotonic phase, appears around 338 K. This result indicates that the increase in the proton mobility above 338 K is closely related with the increase of slope in the temperature dependence of the electrical conductivity around 338 K with increasing temperature. Furthermore a spontaneous strain obtained from the X-ray diffraction data steeply decreases around 338 K. From these results, it is deduced that the increase in the proton mobility above 338 K is caused by the same mechanism as the decrease in the spontaneous strain and yields the proton conductivity observed even below T_c.

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Keywords: Superprotonic conductor; Ferroelasticity; NMR; Proton dynamics

1. Introduction

Zero-dimensional hydrogen-bond crystals $M_3H(XO_4)_2$ (M = K, Rb, Cs; X = S, Se) undergo the superprotonic phase transition from a low-temperature ferroelastic phase to a high-temperature paraelastic phase [1–8]. The $Rb_3H(SeO_4)_2$ crystal, which belongs to these crystals, also shows the interesting features above room temperature; for example, (1) the existence of the ferroelastic phase transition accompanied by the change in the crystal symmetry from the low-temperature monoclinic-A2/a to the high-temperature trigonal-R$\bar{3}$m at T_c (=449 K) [2,3], (2) the superprotonic conductivity (approximately 10^{-2} S/cm) above T_c and (3) the appearance of the electrical conductivity as high as 10^{-5} S/cm observed even below T_c [9–12]. It is known that in the superprotonic phase, superprotonic conductivity of 10^{-2} S/cm results from the hopping motion of a proton accompanied by the breaking and rearrangement of the hydrogen bond by the appearance of the paraelastic property above T_c [5,6,10–14]. On the other hand, the origin of the relatively high electrical conductivity observed even below T_c has not been understood yet. Moreover, the understanding of this origin will be helpful to obtain the important factors required for the appearance of the superprotonic conductivity. Therefore, we have attempted to reveal the origin of the appearance of the electrical conductivity observed even below T_c from the viewpoint of proton dynamics and ferroelasticity by means of the electrical conductivity, ^{1}H-NMR and X-ray measurements.

2. Experimental

$Rb_3H(SeO_4)_2$ single crystals were grown by the slow evaporation method from an aqueous solution of Rb_2SeO_4 and H_2SeO_4 with a molar ratio of $Rb_2SeO_4/H_2SeO_4 = 3:1$ at 308 K. The dielectric constant was measured at a frequency of 1 MHz using an LCR meter (HP 4284A). The ^{1}H-NMR absorption lines were observed in the single crystal by the

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NMR spectrometer with the *Q*-meter detection method. The external magnetic field was applied parallel to *b*-axis. In the present study, the resonance frequency was fixed at 10.6 MHz. The X-ray diffraction patterns were measured at various temperatures using an X-ray diffraction meter (RINT 2000) and lattice constants were subsequently refined.

3. Results and discussion

Fig. 1a shows the ferroelastic domain structure at room temperature in $Rb_3H(SeO_4)_2$. We can frequently observe the domains that consist of three domains D_1, D_2 and D_3 below T_c. The observed angles between the extinction directions of the neighboring two domains separated by the *W* ({311} plane) and *W'*({11n} plane) domain boundaries are given as nearly 120°, where *n* is determined by the strain-stability condition and is therefore generally not an integer. These domain boundaries move by applying the external stress, as shown in Fig. 1a and b. This result indicates that these domains observed in $Rb_3H(SeO_4)_2$ are ferroelastic. Moreover, as shown in Fig. 1c, the domain structure disappears above the ferroelastic phase transition temperature and becomes paraelastic above T_c.

Fig. 2 shows the temperature dependence of the electrical conductivity σ along the *a*-axis in $Rb_3H(SeO_4)_2$. We can clearly see that σ increases with increasing temperature even below the superprotonic phase transition of T_c and increases drastically at T_c. Above T_c, σ becomes approximately 10^{-2} S/cm and thereafter increases with increasing temperature. We also note that the gradient of σ increases above approximately 338 K compared with that below 338 K. This result indicates that the conducting path of carrier or the number of carrier increases above approximately 338 K compared with that below 338 K.

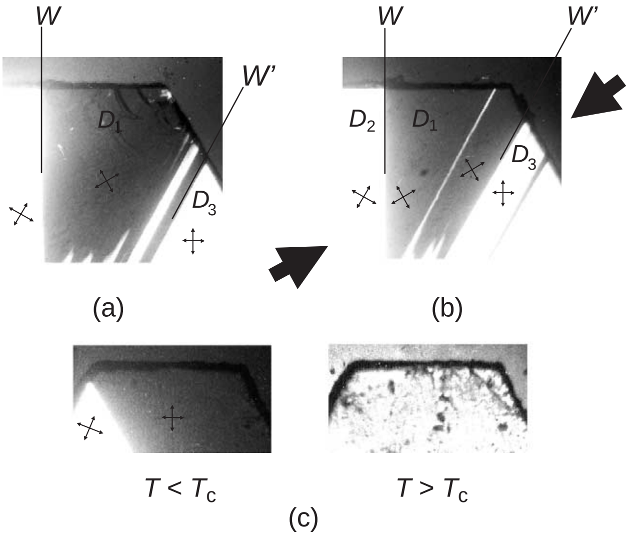

Fig. 1. Domain structure viewed from the a_m–b_m plane of $Rb_3H(SeO_4)_2$: (a) before and (b) after the application of the external stress. The arrow in (b) shows the direction of the external stress. (c) shows the change in domain structure below and above the superprotonic phase transition T_c. The symbol of ⤧ denotes the extinction direction.

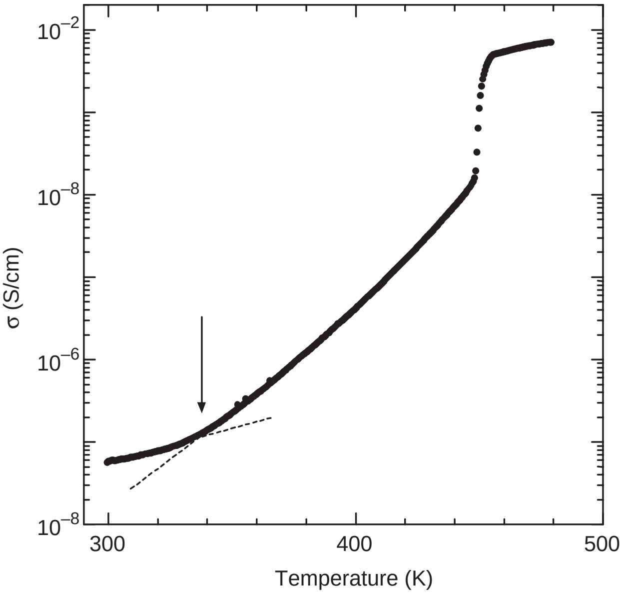

Fig. 2. Temperature dependence of the electrical conductivity σ along the *a*-axis in $Rb_3H(SeO_4)_2$. The slope of the temperature dependence of σ clearly changes around 330 K.

Fig. 3 shows the temperature dependence of the second moment M_2 calculated from the ^{1}H-NMR absorption lines observed at various temperatures using the following equation [15],

$$M_2 = \frac{\int_{-\infty}^{\infty} (H - H_0)^2 f(H - H_0) \mathrm{d}H}{\int_{-\infty}^{\infty} f(H - H_0) \mathrm{d}H}, \tag{1}$$

where H_0 is the resonance magnetic field for ^{1}H-NMR, *H* is the external magnetic field and *f*(*H*) is the measured NMR

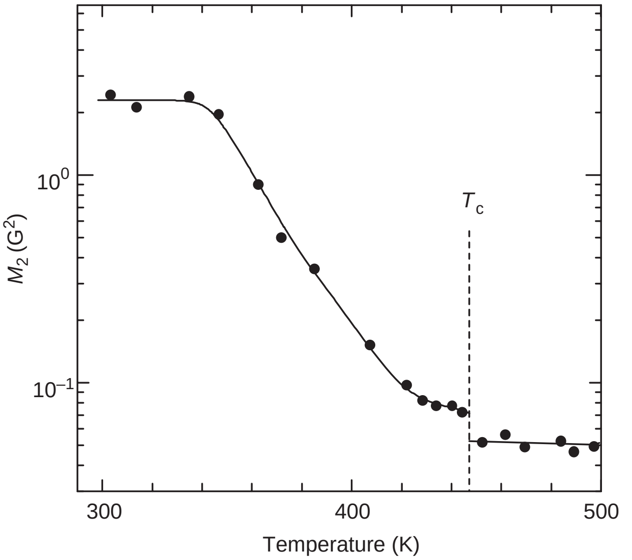

Fig. 3. Temperature dependence of the second moment M_2 in $Rb_3H(SeO_4)_2$. The solid line is a guide for the eyes.