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"Study on the Mechanism of Proton Conductivity in Zero-Dimensional Hydrogen-Bonded Crystals M3H(XO4)2 with M=K, Rb, Cs and X=S, Se"

Part II

presented by:

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Study on the Mechanism of Superionic Conduction in the Zero-Dimensional Hydrogen-Bonded Crystals $M_3H(XO_4)_2$ with M=Rb, Cs and X=S, Se "Part 2" Proton Conduction near and below Tc

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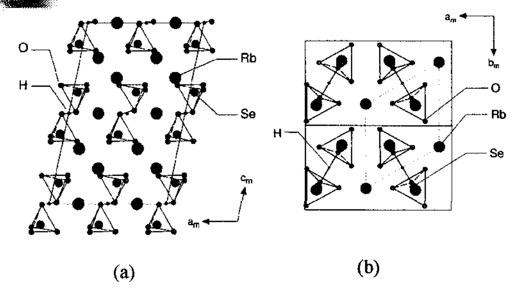
Crystal Structure of $Rb_3H(SeO_4)_2$



(a) (b)

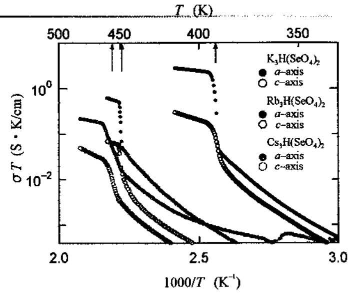
Explanation of the Crystal Structure

- The figure (a) shows a projection of the crystal structure of the ferroelastic phase (T < Tc) on the *a-c* plane.
- We note that the top and bottom oxygen of the neighboring tetrahedrons lie at the same height along the c-axis and that a hydrogen bond is formed in between these top and bottom oxygen.
- These hydrogen bonds are isolated shown here for the ferroelastic phase. Such isolation can be seen clearly in the figure (b), showing a projection of the crystal structure on the *a-b* plane.

Explanation of the Crystal Structure (continue)

- In the paraelastic phase (T>Tc), each tetrahedron is tilted so as for Rb, Se and O to stand in line perpendicular to the *a-b* plane (i.e. *c**-axis).
- As a result a crystal structure in the paraelastic phase has the three-fold axes along the *c**-axis and the length of the hydrogen bonds becomes equal. We call this phase *a super-ionic phase.*
- A unit cell of tetragonal shape in the monoclinic system (T<Tc) changes to a rhombohedral shape surrounded by the red line.
- The space group of the *super-ionic phase* is R3m.

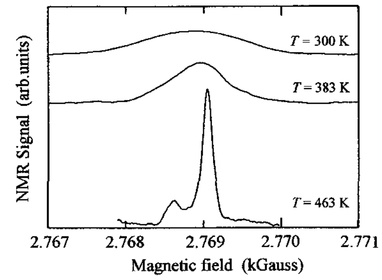
Temperature dependence of electrical conductivity in the $M_3H(SeO_4)_2$ (M=K, Rb, Cs) type crystals



Features of Observed Conductivity in the super-ionic phase (T > Tc)

The slide shows the temperature dependence of electrical conductivity observed for $Rb_3H(SeO_4)_2$.
In the *super-ionic phase* (T > Tc),
(1) log(σT) is proportional to $1/T$, that is the Arrhenius-type conduction.
(2) The conductivity is as high as 10^{-2} to 10^{-4} S/cm.
(3) Conductivity along the *a*- axis is 10^2 times larger than that along the *c*-axis.
(4) Thus $M_3H(XO_4)_2$ crystals display a quasi-two dimensional conduction in the *super-ionic phase.*
(5) The activation energy is about 0.2 eV along the *a*-axis and about 0.4 eV along the *c*-axis.

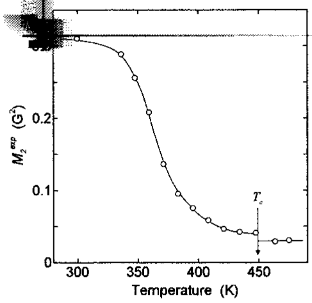
Experimental evidence for coherent motion of proton: ^{1}H-NMR absorption line in $Rb_3H(SeO_4)_2$



Explanation of NMR Data

- This figure shows the ^{1}H-NMR absorption line in the $Rb_3H(SeO_4)_2$ crystal for various temperatures.
- It is evident that the NMR absorption line in the *super-ionic phase* becomes sharper than that at room temperature. The NMR line width in the *super-ionic phase* becomes about 0.3 G, while the line width at room temperature is 1.1G.
- We can say that the sharpening of the NMR line for T>Tc is the motional narrowing effect due to the itinerant motion of proton in the *super-ionic phase* .

Evidence for proton tunneling below T<Tc: NMR second moment M_2 in $Rb_3H(SeO_4)_2$



$$M_2 = \frac{\int_{-\infty}^{\infty}(H-H_0)^2 f(H-H_0)dH}{\int_{-\infty}^{\infty} f(H-H_0)dH}$$

H_0 : Resonance magnetic field for ^{1}H-NMR

H : External magnetic field

$f(H)$: Shape function of NMR absorption line

Explanation of NMR Data

- This figure shows the ^{1}H-NMR absorption line in the $Rb_3H(SeO_4)_2$ crystal for various temperatures.
- It is evident that the NMR absorption line in the *super-ionic phase* becomes sharper than that at room temperature. The NMR line width in the *super-ionic phase* becomes about 0.3 G, while the line width at room temperature is 1.1G.
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Ferroelastic Phase Transition (Ref.: Plakida and Salejda (phys.stat.sol. (b) 148 (1988)473)

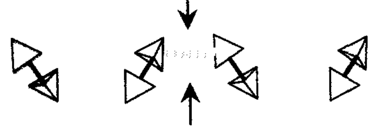
$$F = F_0 + \frac{\alpha}{2}r^2 + \frac{\beta}{4}r^4$$

r: order parameter

$$\alpha = \alpha_0(T - T_c)$$

R_0: distance in T>Tc

r: difference from R_0



Ferroelastic Phase Transition (continue) (Ref.: Plakida and Salejda (phys.stat.sol. (b) 148 (1988)473)

$$T \le T_c$$

$$\frac{\partial F}{\partial r} = 0$$

$$r(T) = \sqrt{\frac{\alpha_0(T-T_c)}{\beta}} = u_0\sqrt{T_c - T}$$

Ferroelastic Phase Transition (continue) Ionic conductivity(No divergence at Tc)

$$\sigma = A\exp\left(-\frac{E(r)}{k_B T}\right)$$

At $T = T_c$, $E(r) \longrightarrow 0$

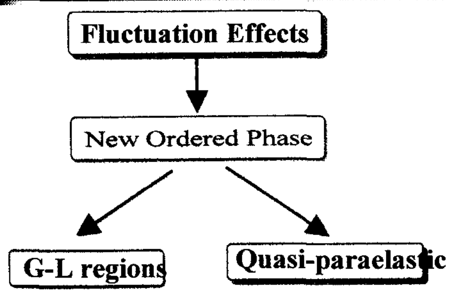
New Idea on the ferroelastic phase near Tc

- **By taking into account the fluctuation effects in the phase transition region just below Tc, we assume that a ferroelastic phase near Tc consists of a mixture of two regions; the quasi-paraelastic regions and the G-L regions**
- .

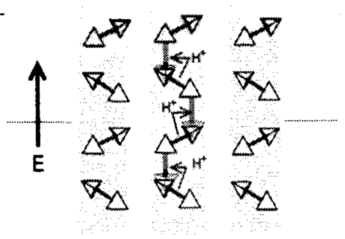
New Idea on the ferroelastic phase near Tc (continue)

- **The quasi-paraelastic region is defined as a region in which the distance between top and bottom oxygen of the neibouring tetrahedrons are nearly the same, while the G-L region is defined as a region in which the (XO_4) tetraherons form a system of dimers connected by the hydrogen bonds.**

Proposal for the region just below Tc



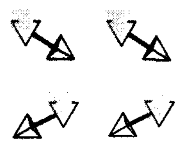
New Ordered Phase Just below Tc



G-L regions

Quasi-paraelestic regions

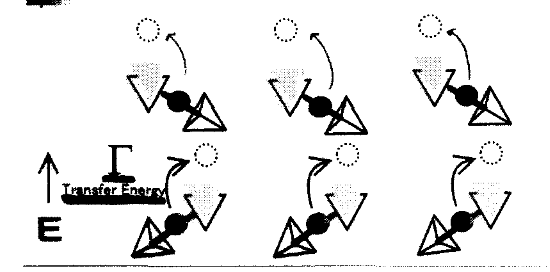
Energy difference between new phase and the mean field phase below Tc



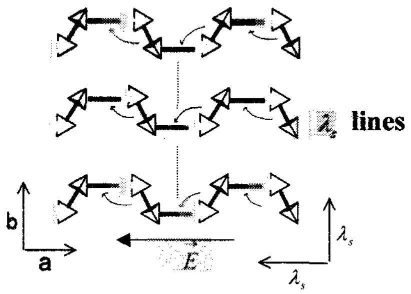
$$\Delta\varepsilon = F_{new} - F_{G-L} \qquad (R = R_0 - r)$$

$$\Delta\varepsilon = \frac{k}{2}(R_0^2 - R^2)$$

Energy gain due to itinerancy of protons



Microscopic view of the quasi-paraelastic regions



Total energy change in the quasi-paraelastic regions

Total energy

$$\Delta E = \frac{k}{2}(R_0^2 - R^2)\lambda_s^2 - a\Gamma \times \lambda_s \quad (1)$$

Determination of λ_s by variational method

$$\frac{\partial(\Delta E)}{\partial \lambda_s} = 0 \quad (2)$$

$$\lambda_s = \frac{a\Gamma}{2kR_0 r - kr^2} \quad (3)$$

near T_c

$$\lambda_s = \frac{a\Gamma}{2R_0 kr} \quad (4)$$

Determination of λ_s by variational method (continue)

Substituting

$r(T) = u_0\sqrt{T_c - T}$ **Into Eq. (4),**

we obtain

$$\lambda_s = \frac{a\Gamma}{2R_0 ku_0\sqrt{T_c - T}}$$

Ionic current and conductivity

By using the expression for mobility in Part 1,

$$I = q\lambda_s\mu = \frac{1.07q^2\tilde{R}^2\Gamma}{\hbar k_B T}\frac{a\Gamma}{2kR_0u_0\sqrt{T_c - T}}E$$

$$\sigma = \frac{1.07\,a}{\sqrt{T_c - T}}\frac{q^2\tilde{R}^2\Gamma^2}{2ku_0R_0\hbar k_B T}$$

Conclusion

- For the ferroelastic transition region just below Tc, we have assumed that a ferroelastic phase near Tc consists of a mixture of two regions; the quasi-paraelastic regions and the G-L regions due to the fluctuation effects.
- As a result the conductivity follows (Tc – T)1/2 power law, consistent with experimental results of ionic conductivity and proton-NMR.