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Dielectric Critical Slowing-Down and Some Related Properties in $RbH_3(SeO_3)_2$

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Dielectric, ultrasonic, thermal and X-ray measurements for $RbH_3(SeO_3)_2$ were made near the ferroelectric transition temperature T_c. $RbH_3(SeO_3)_2$ exhibits anomalies in the ultrasonic velocities and in the specific heat both at $T_i=(2.2°C+T_c)$, the upper transition temperature and T_c. X-ray examinations confirmed an incommensurate nature of the intermediate phase below T_i. The dielectric results obtained above T_c in a frequency range between 3 MHz and 1000 MHz show critical slowing-down of the relaxation time, which is suggested to be originated from discommensuration of the incommensurate phase.

Because of unusual dielectric properties of rubidium trihydrogen selenite, $RbH_3(SeO_3)_2$, such as a small peak of the dielectric constant at the ferroelectric transition temperature T_c and extremely small spontaneous polarization below T_c,[1] many investigations[2–4] have been made to understand its ferroelectric transition mechanism. Dvorak[2] and Sanikov *et al.*[3] analyzed irreducible representations of $RbH_3(SeO_3)_2$ for the ferroelectric phase transition, and the latter authors discussed a possibility of an intermediate incommensurate phase of $RbH_3(SeO_3)_2$ just above T_c. Recently Gladkii *et al.*[5] found a small anomaly in the elastic compliance s^E_{55} at about 2 K above T_c and attributed the anomaly to an incommensurate to the paraelectric (commensurate) phase transition. Very recently Gesi *et al.*[6] made neutron diffraction study of the deuterated crystal $RbD_3(SeO_3)_2$ and reported an incommensurate nature of the intermediate phase.

We have recently measured for $RbH_3(SeO_3)_2$

(1) the ultrasonic velocities of both longitudinal and transverse waves $v_i\,(i=1, 2, \cdots, 6)$ and absorption coefficients α_{ii} $(i=1, 2, 3)$,

(2) the specific heat,

(3) the complex dielectric constant at frequencies below 1000 MHz, and examined

(4) incommensurate nature by the X-ray diffractometer.

The results of (1) and (3) were shortly reported elswhere.[7, 8]

The results of the ultrasonic velocities of the longitudinal waves v_i $(i=1, 2, 3)$ and of the transverse waves v_i $(i=4, 5, 6)$ are shown in Fig. 1. All the ultrasonic velocities v_i's except v_6 show anomalies both at $(2.2°C+T_c)$ and at T_c. In what follows, the temperature of $(2.2°C+T_c)$ is denoted as the incommensurate to the paraelectric (commensurate) phase transition tem-

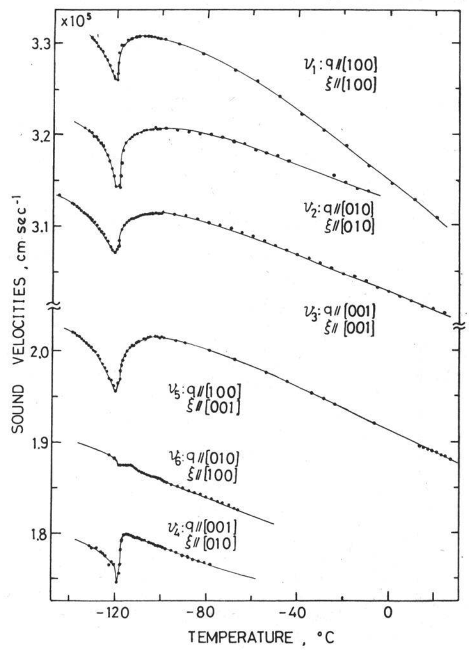

Fig. 1. Sound velocities vs temperature curves. q and ξ show the wave vector and the polarization vector, respectively.

perature T_i, because of the appearance of incommensurate nature of the intermediate phase as will be mentioned below. Figure 2 demonstrates the temperature dependence of v_3 and α_{33} in the very vicinity of T_i, as an example of the results showing the anomalies in v_i's at T_c and T_i. It is noted that the anomalous parts of the observed velocities and absorption coefficients, $\Delta v_i = (v_i^0 - v_i)$ and $\Delta\alpha_{ii}$ $(i=1, 2, 3)$, all show a tendency to diverge at T_i. The normal part of the velocity v_i^0 near T_i is obtained by extrapolating v_i vs T curve in the high temperature range above T_i to low temperature.

The more direct evidence for the existence of the intermediate phase was obtained by the measurement of the specific heat C_p, the result of which is shown in Fig. 3. The total transition entropy ΔS_t associated with both the lower (ferroelectric) and upper (incommensurate to paraelectric) phase transitions was estimated to be 0.12 cal/mol · deg.

The temperature dependence of the real and imaginary parts of the complex dielectric constant along the b axis, ε_b' and ε_b'', measured at various frequencies between 3 MHz and 1000 MHz are illustrated in Fig. 4. The results shown in the figure demonstrate the dielectric dispersion observed near T_c. The real part ε_b' measured at each frequency except 3 MHz and

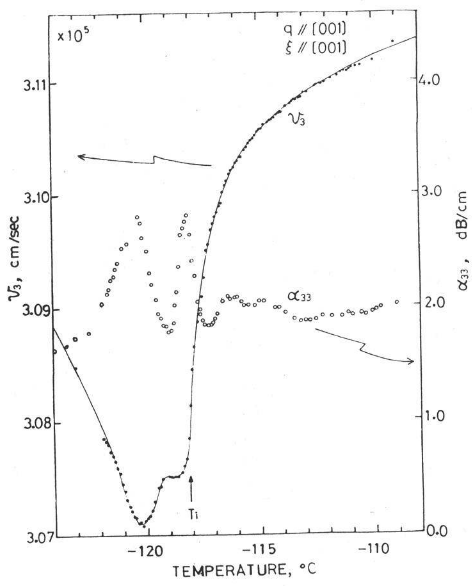

Fig. 2. Sound velocity v_3 and absorption coefficient α_{33} of the longitudinal wave with the wave vector q//[001] and the polarization vector ξ//[001] neat T_i.

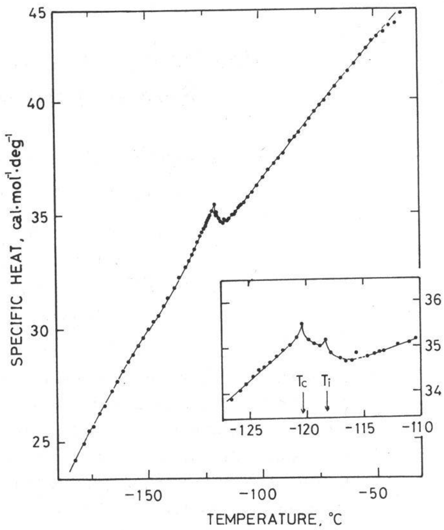

Fig. 3. The specific heat as a function of temperature.

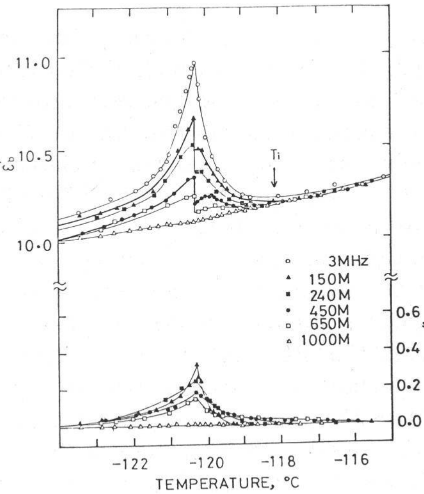

Fig. 4. The real and imaginary parts of the complex dielectric constant, ε_b' and ε_b'', neat T_c.

1000 MHz indicates a discontinuous change in value at T_c, indicating that the ferroelectric transition of $RbH_3(SeO_3)_2$ at T_c is of first order. Examination of the dielectric result by the Cole-Cole relation, $\varepsilon(\omega)-\varepsilon(\infty)=\{\varepsilon(0)-\varepsilon(\infty)\}/\{1+(i\omega\tau)^\beta\}$, indicates that the value of a measure of the width of the distribution of relaxation times, β, falled into a range $0.9<\beta<1$ with uncertainty $\Delta\beta=0.1$. The relaxation time obtained in the incommensurate phase shows critical slowing-down with a value of 1.7×10^{-9} sec just above T_c. However, $RbH_3(SeO_3)_2$ can be regarded as of the displacive type by the observation of a zone-boundary soft phonon mode,[9] for which the dielectric dispersion is expected to arise at frequencies of the order of lattice vibrations. The relaxation frequencies actually observed in $RbH_3(SeO_3)_2$ are too low to attribute to those of the lattice vibrations.

According to McMillan,[10] in the vicinity of T_c in the incommensurate phase the crystal has a domain-like structure with discommensuration. The discommensuration distance increases as T_c is approached from above. It is therefore suggested that the critical slowing-down observed in $RbH_3(SeO_3)_2$ near T_c may be due to the relaxation of polarization contributed from the domain-wall-like movement of discommensuration.

Incommensurate nature of the intermediate phase of $RbH_3(SeO_3)_2$ reported by Gesi *et al.* was confirmed by the X-ray examination. The results of X-ray and neutron[6] diffractions thus support the explanation for the origin of the observed critical slowing-down.

References

1) L. A. Shuvalov, N. R. Ivanov, N. V. Gordeeva and L. F. Kirpichnikova: Sov. Phys.-Crystallogr. **14** (1970) 554.
2) V. Dvorak: Phys. Status Solidi b **51** (1972) K129.
3) D. G. Sannikov and A. P. Levanyuk: Sov. Phys.-Solid State **19** (1977) 67.
4) Y. Makita and S. Suzuki: J. Phys. Soc. Jpn. **36** (1974) 1215.
5) V. V. Gladkii, V. A. Kirikov, V. K. Magataev and L. A. Shuvalov: Sov. Phys.-Solid State **19** (1977) 167.
6) K. Gesi and M. Iizumi: J. Phys. Soc. Jpn. **48** (1980) 697.
7) C. Takei and Y. Makita: J. Phys. Soc. Jpn. **49** (1980) 425.
8) M. Tsukui, M. Sumita and Y. Makita: J. Phys. Soc. Jpn. **49** (1980) 427.
9) H. Grimm and W. J. Fitzgerald: J. Phys. C **11** (1978) 829.
10) W. L. McMillan: Phys. Rev. **B14** (1976) 1496.