^{23}Na spin-lattice relaxation in powder Rochelle salt

© *Cheng Tien*[*], *E.V. Charnaya*[*,**], *M.K. Lee*[*], *S.V. Baryshnikov*[***]

[*] Department of Physics, National Cheng Kung University,
70101 Tainan, Taiwan
[**] Institute of Physics, St. Petersburg State University,
198504 St. Petersburg, Petrodvorets, Russia
[***] Blagoveshchensk State Pedagogical University,
675002 Blagoveshchensk, Russia

E-mail: charnaya@mail.ru

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The temperature dependence of ^{23}Na spin-lattice relaxation in the polycrystalline Rochelle salt was studied by NMR within the range from 235 to 320 K covering both Curie points. The spin-relaxation time t_1 versus temperature curve showed noticeable dips near the phase transitions against the background of the regular decrease in the relaxation time upon increasing temperature. The dips observed were ascribed to critical contributions to sodium spin-lattice relaxation caused by the slowdown of the correlation time for one of two relaxation modes in the Rochelle salt. The ^{23}Na NMR parameters were also measured for the melted Rochelle salt.

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The Rochelle salt (double sodium-potassium tartrate, $\mathrm{NaKC_4H_4O_6 \cdot 4H_2O}$), is the first crystal known to show ferroelectric features. It is generally accepted to have two Curie points, $T_{c1} = 255$ K and $T_{c2} = 297$ K, being ferroelectric in a rather narrow temperature range between T_{c1} and T_{c2} [1]. Both phase transitions are of the second order. The crystalline structure is orthorhombic (space group $P2_12_12_1$) in the paraelectric phases and monoclinic (space group $P2_111$) in the ferroelectric phase. There are four formula units in the unit cell of the Rochelle salt. The spontaneous polarization is directed along the a crystal axis. It is linearly coupled with the ε_4 component of the elastic strain tensor.

According to early theoretical models, based on the structural data in [2], the phase transitions are of the order-disorder type. The spontaneous polarization was attributed to the rotation of the tartrate hydroxyl groups between two equilibrium positions [1]. The two-well potentials for the hydroxyl groups are asymmetric in sush a way that the dipoles form two overlapped sublattices with mirror potentials. Thus, while the dipoles within each sublattice are ordered and the sublattice polarization is nonzero at any temperature, the total polarization can be equal to zero in the paraelectric phases. A phase diagram for sublattices with asymmetric two-well potentials was considered in [3] where it was shown the possibility of occurring the reentrant paraelectric state at low temperatures as in the Rochelle salt (the Mitsui model). Later studies showed that the real situation is more complex and the nature of the phase transitions in the Rochelle salt remains rather unclear. Some experimental facts evidenced the displacive [4,5] or mixed order-disorder and displacive [6,7] type of the phase transitions. Recent x-ray [8] and neutron studies [7] revealed an important role of water molecule displacements. It was also proposed [9] that the order-disorder motion of two hydroxyl groups coupled with the displacive vibrations of water molecules is responsible for the spontaneous polarization and phase transitions. In [10] the Mitsui model [3] was modified taking into account the piezoelectric coupling with the shear strain ε_4.

Since early the Rochelle salt was also studied by NMR [11–14]. From the quadrupole shift of the ^{23}Na NMR levels, the ^{23}Na quadrupole coupling constant was calculated in both paraelectric and ferroelectric states [13]. It was found that all four sodium sites at the paraelectric states are equivalent, while sodium ions form two nonequivalent sublattices through the ferroelectric state. The splitting of the quadrupole coupling constant for two sodium sublattices was proportional to the spontaneous polarization and reached maximum in the middle of the temperature range between T_{c1} and T_{c2}. Contrary to numerous studies of the ^{23}Na NMR line and quadrupole splitting, there were very few publications concerning sodium spin relaxation in the crystalline Rochelle salt and the results were controversial. The existence of anomalies in ^{23}Na spin-lattice relaxation near the Curie points in a Rochelle salt single-crystal was reported in [14]. However, no critical contribution to sodium spin-lattice relaxation was observed in the deuterated Rochelle salt [15]. According to our knowledge, no data were published till now about ^{23}Na spin-lattice relaxation in the powder or polycrystalline Rochelle salt. No data were published about NMR in melted Rochelle salt, either. Here, we present the results of the measurements of the temperature dependences of ^{23}Na nuclear spin-lattice relaxation in the powder Rochelle salt within a temperature range covering both Curie points and in the melt.

1. Experimental

The powder Rochelle salt was purchased from Sigma-Aldrich Co. The announced purity was 99.98%. Nuclear spin-lattice relaxation and the NMR line for ^{23}Na were measured using a Bruker Avance400 NMR pulse spectrometer operating at a Larmor frequence of 105.8 MHz (in magnetic field 9.4 T) within a range from 235 to 320 K. Accuracy of temperature stabilization during measurements was better than 0.5 K. The inversion recovery procedure was applied to observe the restoration of longitudinal nuclear magnetization. To detect the NMR line, a single pulse sequence with phase cycling was used. The repetition time depended on temperature and changed from 10 s at highest temperatures to 30 s at low temperatures following reduction in relaxation rate upon decreasing temperature. The ^{23}Na line position was referenced to a 1 M aqueous NaCl solution. The rate of warming and cooling was very slow to prevent temperature overshoots, which did not exceed 0.1 K in our measurements. Prior to each measurement, the samples were kept at a fixed temperature for about 5 min. Additional measurements for the melt were carried out at 360 K.

2. Experimental results and discussion

The Rochelle salt has large ^{23}Na quadrupole coupling constants in all three crystalline modifications: above, below, and through the ferroelectric state [13]. Because of quadrupole broadening, the satellite transitions in the static ^{23}Na (spin $I = 3/2$) NMR spectrum for the powder Rochelle salt are not observed and the spectrum should show predominantly the central $1/2 \leftrightarrow -1/2$ transition broadened by the second order quadrupole interaction like in other sodium noncubic powder or polycrystalline compounds, for instance, in powder sodium nitrite [16,17]. The line shape obtained within the whole temperature range under study was typical for the central transition additionally broadened by quadrupole coupling with random crystalline electric fields as can be seen in Fig. 1. The temperature dependence of the line shift δ measured as the position of the line peak relative to the reference solution signal is shown in Fig. 2. No noticeable anomalies can be seen near the phase transition temperatures. The linear fit gives a value of the regression coefficient $d\delta/dT = -0.052$ ppm/K.

The ^{23}Na magnetization recovery curves obtained by us can be well fitted with a single exponential. The single exponential recovery was repeatedly observed for many powder crystalline materials (see, for instance, [16] and references therein) and agrees with theoretical predictions for quadrupole relaxation in polycrystalline samples [18]. Thus, relaxation in the powder Rochelle salt can be characterized by a spin-lattice relaxation time t_1. The temperature dependence of t_1 is shown in Fig. 3.

The t_1 versus temperature curve shows noticeable dips near both Curie temperatures (Fig. 3). The dips observed revealed the existence of an additional critical contribution to sodium spin-lattice relaxation against the background of the decrease in the relaxation time with increasing temperature. Such a critical contribution to spin relaxation was discussed in [15,19] for both types of ferroelectric phase transitions, order-disorder and displacive. The increase in the spin-lattice relaxation rate at the order-disorder phase transitions was ascribed to the critical slowdown of the order parameter relaxation time. Theoretical treatments of dynamics in the Rochelle salt performed in [9,20] showed that it exhibited the two-mode relaxation behavior, the correlation time of one of these two modes slows down on approaching the two Curies points in agreement with dielectric and acoustic data. It was shown in [15] using the classical spectral density description of spin-lattice relaxation that the relaxation rate should behave near the transition temperature as $(T-T_c)^{-1/2}$ or as $\ln(T-T_c)$ for isotropic

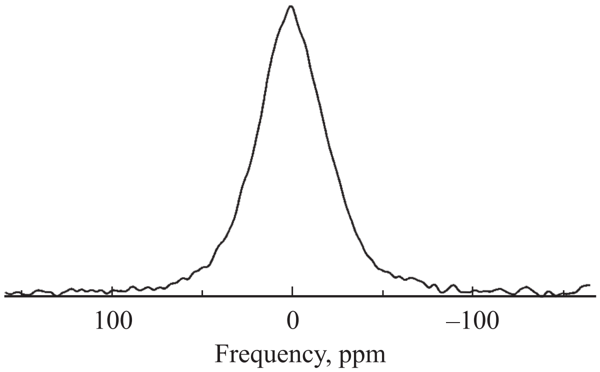

Figure 1. ^{23}Na NMR line shape in the powder Rochelle salt at 298 K.

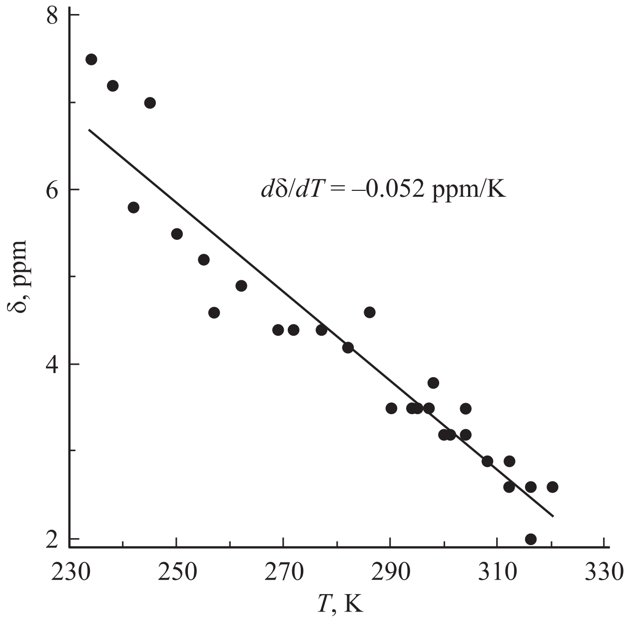

Figure 2. Temperature dependence of the ^{23}Na NMR line shift in the powder Rochelle salt.

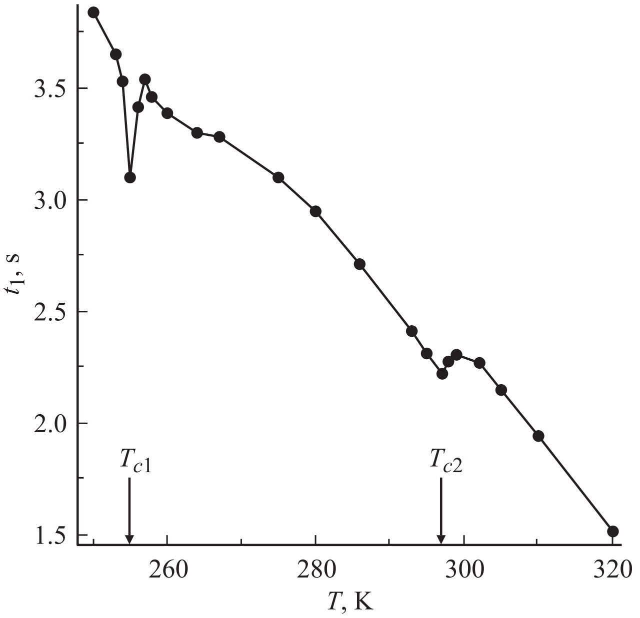

Figure 3. Temperature dependence of the ^{23}Na spin-lattice relaxation time in the powder Rochelle salt.

and anisotropic dipole interactions, respectively. In general, this approach allows explaining the ^{23}Na t_1 measurements in the powder Rochelle salt, while the precise temperature dependence of the critical contributions to relaxation cannot be found because of comparably small critical t_1 anomalies. Background spin-lattice relaxation is mainly caused by the Raman two-phonon quadrupole interaction [21], which is known to dominate at moderate temperatures in insulator crystals. Small admixture of relaxation due to paramagnetic impurities also can contribute to the background T_1 as in sodium nitrite [22], sodium chlorite, and other crystals [21].

The results for the powder Rochelle salt can be compared with those obtained for a single crystal oriented in such a way as to have the best superimposition of the central and the satellite lines [14]. All transition lines were irradiated under that orientation and restoration of the total spin magnetization was observed contrary to the conditions of the present experiments. There are some clear differences between spin-lattice relaxation in single crystalline and powder samples. While maximal critical contribution at T_{c1} is about the same in both samples, the temperature ranges of the observed critical anomalies near both phase transitions in the single crystal are more than twice as broad as in the powder sample and the critical dip at T_{c2} is noticeably smaller in the powder sample. Besides, we did not observe sharp increase in the relaxation rate above 310 K which the authors of [14] associated with random flipping motion of the water molecules. One can suggest that the latter discrepancy can rise due to difference in the quality of the samples studied.

Upon further warming the powder sample, one can observe above 350 K a signal from the „melted“ Rochelle salt [1]. The melting offset was seen near 360 K. At that temperature the integral intensity of the ^{23}Na NMR line was by a factor of 2.4 greater than at 295 K since all transitions can be irradiated when the Rochelle salt becomes liquid in agreement with theoretical predictions [21] and the linewidth decreased to about 10 ppm in contrast ot the solid Rochelle salt line (Fig. 1). The spin-lattice relaxation time measured for the Rochelle salt melt at 360 K was 19 ms. The chemical shift for the melted Rochelle salt at 360 K referenced to the NaCl solution was equal to 3.5 ppm.

In conclusion, our ^{23}Na NMR studies of the polycrystalline Rochelle salt revealed pronounced critical contributions to spin-lattice relaxation near both Curie points. No noticeable critical anomalies were seen for the NMR line shift. The temperature dependence of the spin-lattice relaxation time showed some differences compared to that for the single crystalline sample. The NMR line shape, chemical shift, and relaxation time were also measured for melted Rochelle salt at 360 K.

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