

## Resonant soft mode in Rochelle salt by inelastic neutron scattering

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Inelastic neutron-scattering study of a deuterated crystal of Rochelle salt confirms the existence of a resonant mode near  $25\text{ cm}^{-1}$  at 50 K which softens with increasing temperature and becomes overdamped on approaching the phase transition to the ferroelectric phase. We argue that this mode is the regular soft mode of the ferroelectric phase transition. The analysis of the inelastic neutron-scattering structure factors allows us to conclude that the soft mode eigenvector involves mainly relative displacements of the same three molecules of crystal water, which were found in recent structural studies to show the largest static displacements in the ferroelectric distortion. Weak phonon dispersion along the  $a^*$  and  $b^*$  axes leads us to predict the existence of another resonant mode with a similar frequency and displacement pattern but having a different symmetry.

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Rochelle salt (RS), *sel de Seignette (1675)* or the sodium potassium tartrate ( $\text{NaKC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$ ) is the first substance shown to be ferroelectric.<sup>1</sup> Up to now it appears as the only system with a re-entrant paraelectric phase: the  $C_2^2$  ( $P2_111$ ,  $Z=4$ ) ferroelectric phase is plunged in the  $D_2^3$  ( $P2_12_12$ ,  $Z=4$ ) paraelectric phase, so that there are two Curie points ( $T_1=255\text{ K}$  and  $T_2=297\text{ K}$ ). Explanation of this curiosity has motivated a number of studies,<sup>2-5</sup> while others searched to find quantitative differences between the two paraelectric phases which may justify quite alternative models.<sup>6,7</sup>

In any case the microscopic insight in the phase transition mechanism is still missing. One of the reasons is that the crystal structure is rather complicated and that the structural distortion in the ferroelectric phase is rather small. Originally, it was proposed that the principal displacement is due to ordering of the hydrogen bonds between the O1 and O10 oxygen atoms<sup>8</sup> (hereafter we use the atom labels of Ref. 8, viz. Fig. 1), which happens to be parallel to the direction of polarization ( $x$ ). Soon after this proposition was ruled out<sup>9</sup> and the role of the hydroxyl hydrogen of the O5 oxygen was considered as principal.<sup>10</sup>

Since then the structural model was significantly improved. The structural studies reported in the last decade<sup>11,12,6</sup> firmly established that the largest displacements induced by the phase transition are those of the water molecules associated with oxygens O8, O9, and O10. Nevertheless, in further details differences still persist between the reported structural models. For example, the recent x-ray study of the ferroelectric phase in a monodomain sample<sup>12</sup> seems to show additional displacements of the carboxyl group O3-C4-O4. The structural data in the most recent x-ray powder-diffraction study<sup>6</sup> shows a surprisingly large displacement also for the C1 atom (so that rotation of whole tartrate molecules is finally assumed), while the split atom model of the paraelectric phase based on neutron diffraction data<sup>11</sup> suggests that the O5 hydroxyl group may still play some role in the phase transition.

The order parameter dynamics seems also somewhat complex in this material. Originally, the phase transition of RS was attributed to the order-disorder type, due to the pronounced critical slowing down of a Debye relaxation mode

in the GHz region observed in the vicinity of both  $T_1$  and  $T_2$ .<sup>13-15</sup> Later on, dielectric measurements in the submillimeter region have shown a resonant lattice mode near  $22\text{ cm}^{-1}$  that becomes soft and overdamped on approaching the phase transition from below,<sup>16</sup> indicating clearly the displacive feature of the phase transition. Subsequent dielectric measurements in the GHz region<sup>17</sup> have established the coexistence of the soft mode with the relaxation mode in a large temperature region (between 100 and 300 K at least, see also Ref. 19). These results prove that the overdamped response of the lattice mode is not identical to the previously seen Debye relaxation. Such situation, where the soft mode is complemented by a relaxational mode, is typical for the systems which are at the crossover between order-disorder and displacive mechanism. The relaxational mode is then not counted among the  $3N$  normal vibrations of the lattice, since the atomic displacement pattern associated with both modes is essentially the same (differing only by the amplitude).<sup>16</sup>

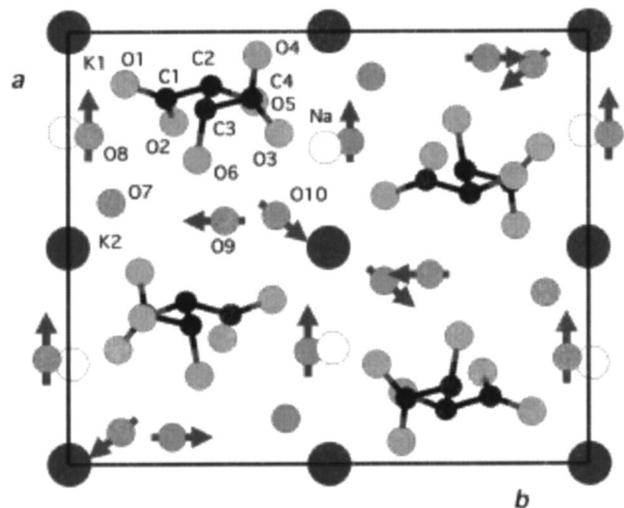


FIG. 1. Projection of the unit cell of Rochelle salt crystal on the  $a$ - $b$  plane with atom labels of Ref. 8. The arrows show the displacement pattern of the soft mode, as evidenced by this study (schematic, see text).

In addition, in order to explain a rather strong temperature dependence of the dielectric strength of the observed mode,<sup>18</sup> it was proposed that this soft lattice mode is bilinearly coupled to another hypothetical soft mode at higher frequency. Actually, a mode which may play such a role was really found in the subsequent far-infrared spectroscopic investigations.<sup>19</sup> More precisely, it was found that the experimental data can be interpreted assuming a bare hard mode at  $37\text{ cm}^{-1}$  with zero dielectric strength bilinearly coupled to a bare mode with temperature-dependent frequency ( $74.3\text{ cm}^{-1}$  at 50 K,  $68.3\text{ cm}^{-1}$  at 240 K), via a temperature-independent coupling constant of  $2128\text{ cm}^{-2}$ . As a result of this coupling, the lower eigenmode reproduces the observed temperature dependence of the frequency and dielectric strength. Nonetheless, the eigenvector change between 50 and 240 K calculated from this model does not exceed a few percent. Thus we believe that even though the explanation of the temperature dependence of the frequency, damping, and dielectric strength may require some harmonic or anharmonic coupling mechanism, the temperature changes of the lowest frequency mode eigenvector are actually quite small. Consequently, we suggest that the eigenvector of the resonant lattice mode with frequency near  $22\text{ cm}^{-1}$  should be responsible for the essential part of the structural displacement of the ferroelectric phase, and we will refer to it simply as to *the soft mode* of the RS.

In this short paper we report on the inelastic neutron-scattering study of this soft mode. To reduce the incoherent scattering background, we have used a partially deuterated crystal<sup>16</sup> of about  $2\text{ cm}^3$  in which the hydrogen atoms of the hydroxyl groups and water molecules were replaced. The measurements were carried out on the IN3 and IN12 three-axis spectrometers (TAS) at the Institute Laue-Langevin (Grenoble, France). The first part of the experiment, whose aim was to localize the resonant mode, to explore its dispersion within the Brillouin zone and to follow the thermal variation of its damping, was carried out on the cold neutron TAS IN12. The instrument was operated in the  $Q=\text{const.}$  mode with  $k_f=1.5\text{ \AA}^{-1}$ . We have used a vertically focusing graphite monochromator (PG002) followed by a 40' Soller collimator and a fully focusing PG002 analyzer in an open geometry, combined with a beryllium filter.

Figure 2 shows the temperature variation of the soft mode spectra in the low-temperature paraelectric phase, measured in the 050 Brillouin zone. For comparison, the expected spectral profile of this soft mode is shown in the Fig. 3. These profiles correspond to the response function  $f(\omega)$  of a damped harmonic oscillator with the oscillator frequency  $\omega_0$  and the damping constant  $\Gamma$  taken from the previous submillimeter dielectric measurements on nondeuterated RS,<sup>18</sup> multiplied by the Bose-Einstein temperature factor, i.e.,

$$f(\omega)=[n(\omega)+1]\text{Im}\left[\frac{1}{\omega^2-i\omega\Gamma-\omega_0^2}\right]. \quad (1)$$

Deuterated RS is known to have only slightly different properties, for example the temperature interval of the ferroelectric phase is somewhat larger (with  $T_1=251\text{ K}$  and  $T_2=308\text{ K}$ ).<sup>5</sup> The measurements between 90 and 190 K have

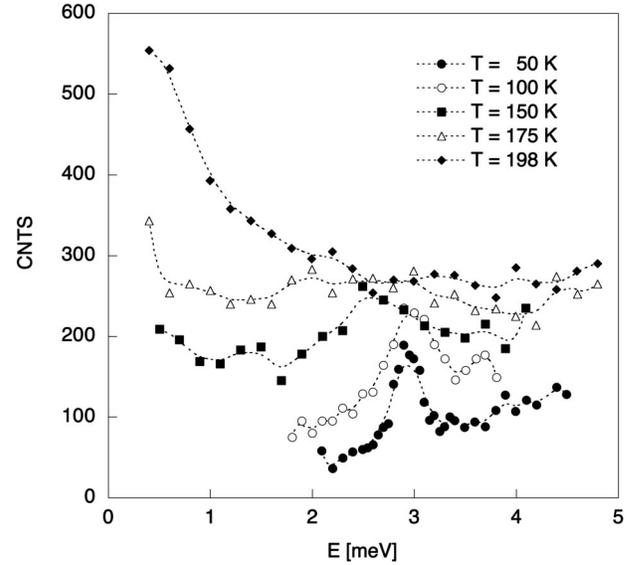


FIG. 2. Inelastic neutron-scattering spectra measured in the 050 zone center for different temperatures.

shown that the soft-mode frequency of deuterated RS is a few percent higher but otherwise all the soft mode behavior remains unchanged.<sup>16</sup> As expected, the results in Fig. 2 are quite similar to the calculated profiles of Fig. 3, apart from this small isotopic shift. Taking into account the temperature dependence of the background coming probably from both the coherent and incoherent scattering, there is no big difference between temperature evolution of the overall intensity in Figs. 2 and 3. This means that the possible temperature dependence of the inelastic neutron-scattering structure factor is negligible. It partly corroborates our claim about rather small temperature changes in the soft mode eigenvector.

For further characterization we have also checked the dis-

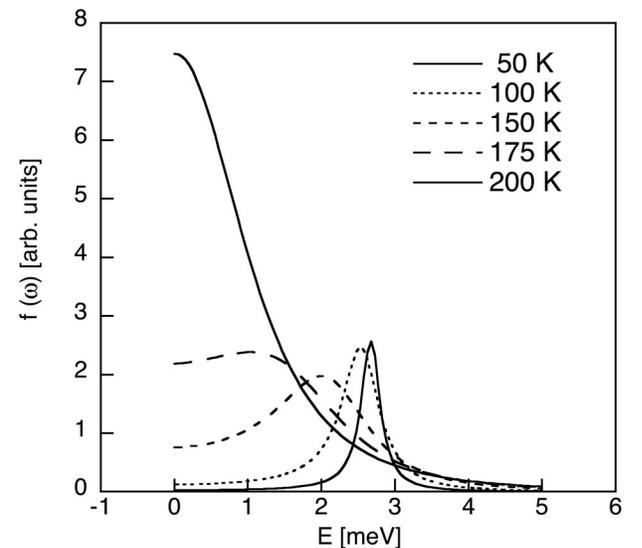


FIG. 3. Simulated response function of the soft mode in Rochelle salt, as expected to appear in the inelastic neutron-scattering spectra. The curves correspond to temperatures of 50, 100, 150, 175, and 200 K.

persions of the soft mode along the two principal directions  $a^*$  and  $b^*$ . The dipole moment of the soft mode is oriented along the  $x$  axis, so that the two dispersion curves may extrapolate to two different frequencies  $\omega_{LO}$  and  $\omega_{TO}$ . However, we could not observe such LO-TO splitting which means that  $\omega_{LO} - \omega_{TO}$  is smaller than 0.2 meV. This is in agreement with the rather small dielectric strength found in the optical investigations.<sup>19</sup> The overall dispersion in the Brillouin zone is less than 10%, showing that the soft mode belongs to a flat optical branch. It may be thus expected that there exists at least one other mode of about the same frequency, similar displacements but opposite phase between some of the symmetry related formula units, and thus of different symmetry. Search of the antiphase mode by low-frequency Raman spectroscopy is now in progress.

The essential advantage of inelastic neutron scattering is the access to the information about the phonon eigenvector via one-phonon structure factors. For this reason, we have measured the scattering intensity due to the soft mode at 50 K in the  $\Gamma$  points of about 80 different Brillouin zones in the  $hk0$  plane. Among them, the Brillouin zones 800, 390, 190, 050, 540, 580, 070, and 044 have shown the strongest signal. Part of these measurements was carried out on the IN3 TAS at a thermal neutron guide, providing access to a larger range of the reciprocal space. In order to avoid the strong background due to inelastic scattering of the  $\lambda/2$  neutrons, we have worked with a filtered incident beam at constant  $k_i = 2.662 \text{ \AA}^{-1}$  (graphite filter). The energy of the scattered neutrons was analyzed by a horizontally focusing analyzer using bent perfect Si 111 crystals. In agreement with the selection rules<sup>22</sup> imposed by the  $B_3$  symmetry of the soft mode, we have observed this mode neither in the Brillouin zones  $0k0$  with  $k$  even nor in the  $h00$  Brillouin zones with  $h$  odd. Obviously, the collected intensity data are not sufficient to determine completely the soft-mode eigenvector for a structure with 28 atoms in an asymmetric unit cell. Nevertheless, the analysis of the relative scattering intensities in the even  $h00$  and odd  $0k0$  Brillouin zones provides some insight into the most important displacements along the  $x$  and  $y$  directions, respectively.

In the case of the  $0k0$  reflections, we have observed that the soft-mode signal is clearly the strongest in the 050 Brillouin zone. Note that the 050 Bragg reflection is just the strongest one among the odd  $0k0$  Bragg reflections (both x-ray and neutron) that appear in the ferroelectric phase<sup>21</sup> and its intensity is directly proportional to the square of the polarization.<sup>21</sup> Such coincidence is in a good agreement with our claim that the eigenvector of the observed mode corresponds to the order parameter.

The inelastic neutron-scattering structure factor for the one-phonon scattering<sup>22</sup> on a  $B_3$  mode in an odd  $0k0$  zone can be written as

$$F(0k0) = 4 \sum b_\mu(u_{\mu,y}k) \cos(2\pi ky_\mu) \exp[-W_\mu(k)], \quad (2)$$

where  $b_\mu$  is the coherent neutron-scattering length for atom  $\mu$ ,  $u_{\mu,y}$  is the displacement of atom  $\mu$  along the direction  $y$ ,

usually associated with a normalized mass-reduced eigenvector of a dynamical matrix  $[u_{\mu,y} = m_\mu^{-1/2} e_y(\mu, q=0)]$ ,  $\exp[-W_\mu(k)]$  is the Debye-Waller factor,  $y_\mu$  is the relative positional  $y$  coordinate of the atom  $\mu$  with respect to the position of the twofold axis  $C_2(z)$  and the summation is assumed to be performed over all atoms in an asymmetric unit cell with a single formula unit. The above expression coincides with the expression for the usual (static) structure factor of the  $0k0$  Bragg reflection in the ferroelectric phase, provided that the  $u_{\mu,y}$  are replaced by the components of the ‘‘frozen’’ ferroelectric distortion.

According to all recent structural studies,<sup>12,6,11,20</sup> the largest static  $y$  displacements in the ferroelectric phase are found for the water oxygen atoms O9 and O10, and these displacements are in a mutually opposite sense. We have verified that the 050 reflection intensity is practically determined by the contributions of O9 and O10 atoms only. This special situation arises because the relative  $y$  coordinates of these oxygen atoms are accidentally very close to the subsequent multiples of  $1/10$  ( $3/10$  and  $4/10$ ). That is why the  $\cos(2\pi ky_\mu)$  factor in Eq. (2) just changes the sign of the O9 contribution and displacements of both oxygen atoms are summed up to produce a large total structure factor. This fortunate combination is partly lost in the case of the neighboring odd reflections, where the contributions of O9 and O10 oxygen atoms get diminished by the phase factor. In the case of neutron scattering on deuterated RS one has to consider also the contributions of deuterium atoms attached to O9 and O10. However, when assuming that these  $D_2O$  molecules displace as whole, almost the same results are obtained.

The presently observed clear superiority of the 050 over all other  $0k0$  phonon scattering intensities is enough for an analogous conclusion: The antiphase shifts of the O9 and O10 water molecules in direction  $y$  give the principal contributions among the  $y$  components ( $u_{\mu,y}$ ) of the soft mode eigenvector.

Quite analogously, the one-phonon structure factors in  $h00$  positions allow to analyze the displacements in the  $x$  direction. This direction is even more interesting since it corresponds to the direction of the spontaneous polarization in the ferroelectric phase. Here the soft-mode scattering is the strongest in the 800 Brillouin zone (it has actually the strongest intensity among all investigated zone centers). Clearly, the problem with displacements along the  $x$  direction is more complex than in the  $y$  direction. First of all, there are no new Bragg reflections induced by the phase transition. Second, the previous structural studies have proposed that the ferroelectric distortion may include displacements along the  $x$  direction for a number of different atoms.<sup>11,6,12</sup> In fact, the 800 intensity can be accounted for just by assuming the mutually opposite displacements of O8 and O10 water molecules, which show largest displacements in the  $x$  direction according to the two most recent structural studies.<sup>6,12</sup> It turns out that the  $x$  coordinates of the oxygen atoms O8 and O10 are again close to even and odd multiples of  $1/16$ , respectively (near  $4/16$  and  $1/16$  in this case), which is favorable for summing up their contributions to the 800 structure factor if their displacements go in the opposite sense. Thus we believe that the antiphase shift of the O8 and O10 water mol-

ecules in the  $x$  direction, observed in the ferroelectric displacement, has a counterpart in large and opposite values of  $x$  components ( $u_{\mu,x}$ ) of the soft-mode polarization vectors belonging to the water molecules associated with O8 and O10, respectively. These findings clearly support our conjecture about the soft-mode character of the investigated phonon mode. Obviously, the additional small  $x$  components ( $u_{\mu,x}$ ) not revealed here may bear the above-mentioned temperature dependence of the dielectric strength,<sup>18</sup> or may turn out to be in another way important for the complete understanding of the phase transition mechanism. However, the experimental data of this study does not allow us to establish the phonon eigenvector in more detail.

The present results provide a link between previous structural and spectroscopic investigations: It was established that the resonant soft mode (near  $22\text{ cm}^{-1}$  at 50 K in nondeuterated RS), which becomes overdamped near the phase transition, involves a correlated motion of three of the four crystal water molecules. These are the same three water molecules which are known to contribute most significantly to the static ferroelectric displacement (see Fig. 1). As in the static displacement, the largest displacement in the  $x$  projection are

due to the out of phase vibration of the O8 and O10 water molecules, while in the  $y$  projection the largest vibrational amplitudes correspond to the out of phase vibration of the O9 and O10 water molecules. All these findings supports our claim that the investigated  $22\text{ cm}^{-1}$  resonant mode plays the role of the soft mode. Further, it was found that the soft mode belongs to a rather flat optic branch, which is in agreement with the order-disorder aspects of the phase transition [as, for example, in  $\text{Sn}_2\text{P}_2\text{S}_6$  (Ref. 23)]. Due to the nonsymorphic symmetry of the structure, this also strongly favors the existence of at least one other zone-center mode of different symmetry (“Davydov-splitting-type” partner). Complementary elastic neutron-diffraction study in the ferroelectric phase which would allow to extract the complete symmetry breaking distortion including the displacements of deuterium atoms is under preparation.

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