

Phase-transition mechanism in  $\text{RbH}_2\text{PO}_4$ -type ferroelectrics

Patrick Simon and François Gervais

*Centre de Recherches sur la Physique des Hautes Températures, Centre National de la Recherche Scientifique, F-45045 Orléans, France*

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The temperature dependence of polar phonon spectra of  $\text{RbH}_2\text{PO}_4$  for the electric field polarized parallel to the ferroelectric axis is reported. The phonon responses are deduced from the best fit of the factorized form of the dielectric function to infrared reflectivity data. Results show softening of the main  $\nu_{4c}$  mode, destabilized by the order-disorder phenomenon of intersite proton motions. This  $\nu_{4c}$  soft mode couples with lower-frequency external modes and induces the ferroelectric phase transition.

The nature of the lattice excitations that trigger the ferroelectric (FE) phase transition in KDP-type (KDP denotes potassium dihydrogen phosphate) crystals is one of many exciting questions that remains open to discussion even after decades of extensive investigation. The analysis of the temperature dependence of infrared reflection spectra of  $\text{RbH}_2\text{PO}_4$  recorded with a modern repetitive Fourier spectrometer, reported in the present paper, provides direct observation of the vibrational modes involved in the ferroelectric phase transition and their contribution to the dielectric constant. Results shed new light about the mechanism of the phase transition in a simple and unambiguous way, thus solving long-standing puzzles and controversies.

To explain the FE phase transition within an eventual displacive mechanism picture, we have to search for a polar-soft transverse-optical (TO) mode with eigenvectors along the FE axis, and the discussion throughout this paper will be restricted to this polarization. Raman, Brillouin, and neutron scattering experiments (see bibliography in recent review papers, Refs. 1–3), agree with respect to observation of a “central peak” which extends up to  $100\text{ cm}^{-1}$  near the Curie temperature  $T_C$ . Peercy<sup>4</sup> has shown the character of a propagating mode of this low-frequency response in KDP since it becomes a well-defined *underdamped* vibrational mode under high pressure. Recently, however, Tokunaga and Tatsuzaki<sup>3</sup> focused attention on the following fundamental problem: if the central component is assigned to an overdamped TO mode, the presence of another neighbor—unambiguously external—TO mode (at  $150\text{ cm}^{-1}$  in the paraelectric phase of  $\text{RbH}_2\text{PO}_4$ ), seems inconsistent with group-theory analysis that predicts only one low-frequency external mode for this polarization. Such a mode consists of the vibration of K (Rb) ions against  $\text{PO}_4$  molecular groups (Fig. 1). The argument that the central component cannot be the symmetry-allowed low-frequency external mode of the paraelectric (PE) phase is confirmed on inspection of the generally accepted picture of the static displacements of ions that occur at the phase transition:<sup>5</sup> as the two protons of the “upper” H–O bonds of the  $\text{PO}_4$  group move to sites near both upper oxygens (pushing each oxygen towards the other), the two protons in the “lower” bonds move away (leaving both lower oxygens free to increase their distance), the P ion moves down along the FE axis, and the K (Rb) ions move up. Such motions do not fit an external-mode configuration owing to the oxygen displacements that are perpendicular to the FE axis, whereas they should necessarily vibrate against cations to yield an instan-

aneous dipole moment along the FE axis. (The mode of which the eigenvectors are the same as the static displacements of atoms that occur at  $T_C$ , is commonly called the “polarization-fluctuation” mode.) The only other symmetry-allowed external modes for this polarization in the PE phase are proton-bending modes, motions that, in  $\text{RbH}_2\text{PO}_4$ , are perpendicular to the so-called proton-tunnel mode. Their frequency is expected to lie above  $1000\text{ cm}^{-1}$ , due to the very low proton mass. The natural questions that arise then are the following. Do the intersite protonic-relaxational motions that are, in practice, perpendicular to the FE axis in  $\text{RbH}_2\text{PO}_4$ , play any role in the FE phase transition and if they do, as this is generally believed owing to the drastic changes induced by deuteration, by which mechanism? How can the results of group-theory analysis and the low-frequency *extra* mode (which is generally assigned to polarization fluctuation) be reconciled?

The temperature dependence of the TO-mode response for the electric field of infrared radiation polarized parallel to the FE axis is shown in Fig. 2. Results were deduced from the best fits of the factorized form of the dielectric

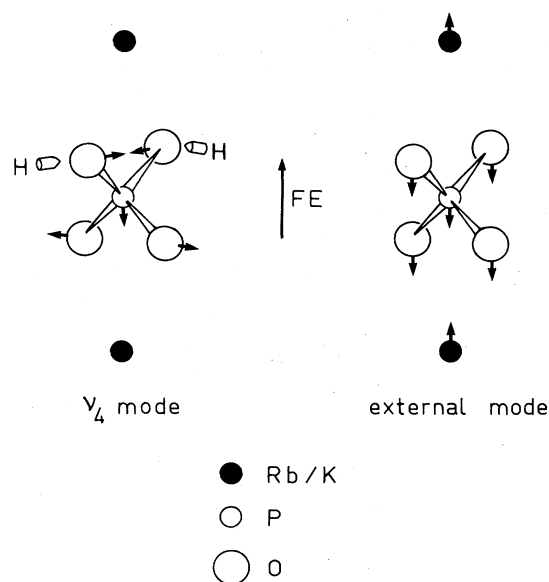


FIG. 1. Schematic representation of eigenvectors of internal  $\nu_4$  and external-vibration modes at the Brillouin-zone center.

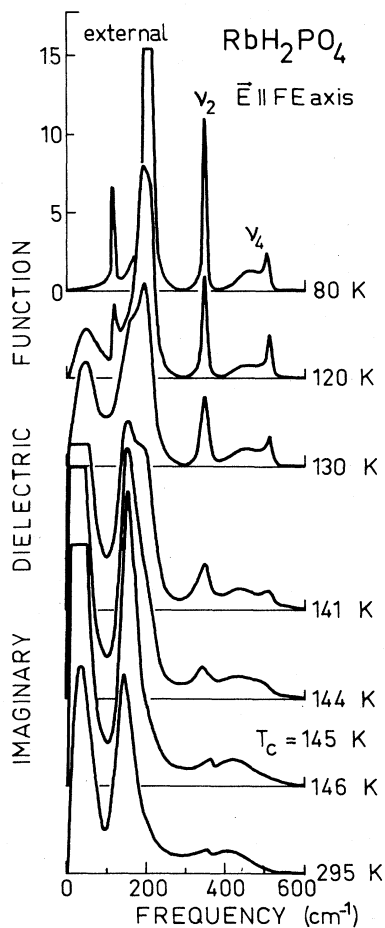


FIG. 2. Temperature dependence of TO-vibration modes in the FE and PE phases of RbDP.

function to reflection spectra obtained from 20–4000  $\text{cm}^{-1}$ , a procedure now standard as detailed in Ref. 6. Our infrared reflectivity data agree with earlier recordings.<sup>7,8</sup> This is, however, the first time that a set of *complete* spectra are fitted with a dielectric-function model over the appropriate temperature range. The model is very simple in that it involves only two adjustable parameters (frequency and damping), per transverse- or longitudinal-optical mode, but also powerful since it is able to reproduce asymmetric lines without adding coupling parameters, as explained in Ref. 6. An example of data fit is shown in Fig. 3. Results also agree with those of Kramers-Kronig inversion. Figure 2 shows that the imaginary part of the dielectric function vanishes between 550  $\text{cm}^{-1}$  and the  $\nu_3$ -mode region (around 1000  $\text{cm}^{-1}$ ). High-frequency modes, therefore, are decoupled from those plotted in Fig. 2 and they may be forgotten in the present discussion.

At 80 K, the  $A_1$  spectrum consists of two external modes (plus one merged into the most intense line and better observed at higher temperature), then one  $\nu_{2c}$  and two  $\nu_{4c}$  internal modes (Herzberg's notation), all symmetry allowed. Such assignments are straightforward by comparison with the frequencies of the  $\text{PO}_4^{3-}$  ion.<sup>9</sup> All modes but the most intense  $\nu_{4c}$  are weakly damped. The most-damped  $\nu_{4c}$  mode shifts down while its intensity together with its linewidth in-

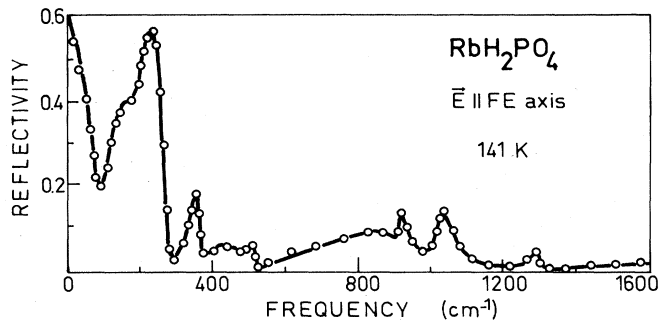


FIG. 3. Typical infrared reflection spectrum (dots), of RbDP just below  $T_C = 145$  K, and best fit (full line) to the data with the factorized form of the dielectric function.

creases rapidly upon heating towards  $T_C$ , as also shown in Fig. 4. The lowest-frequency component also seen in scattering spectra starts appearing above 100 K. It may be described as a slightly overdamped TO mode, the frequency of which shifts down while its intensity increases drastically upon heating below  $T_C$ . The phenomenon is reversed above  $T_C$  and the picture appears fully compatible with a soft-mode-induced phase-transition mechanism. A number

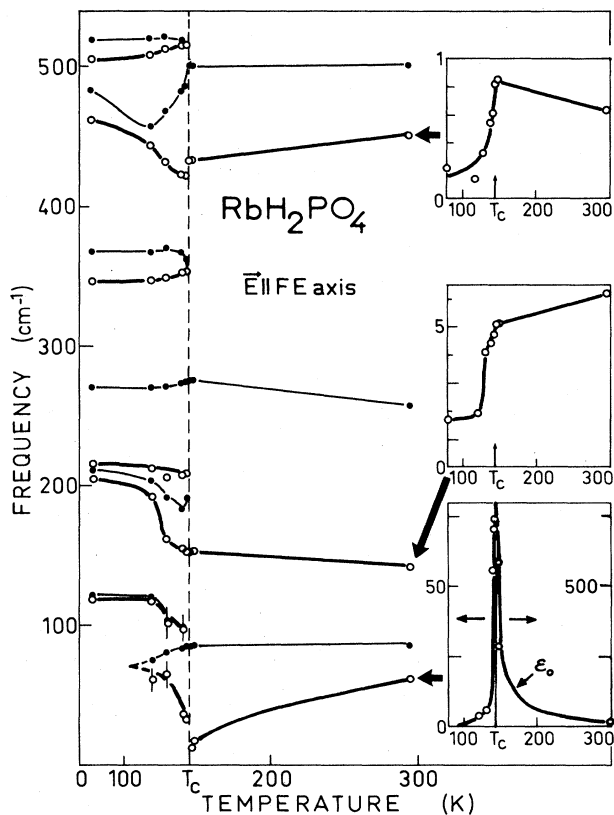


FIG. 4. Temperature dependence of TO (open circles connected by heavy lines) and LO (full circles connected by thin lines) modes in RbDP. Inserts show the temperature dependence of the oscillator strengths of the three main TO modes, deduced from TO-LO splits (Ref. 6). Results for the soft mode in the PE phase are compared with the static-dielectric constant (Refs. 13 and 14) (full line).

of modes (two external and one  $\nu_{4c}$  mode) vanish at  $T_C$  according to symmetry predictions. The remaining external mode softens partially in the FE phase due to coupling with the upper  $\nu_{4c}$  soft mode and its line shape is characteristic of strong interference with the lowest-frequency overdamped mode that plays the role of a broad continuum, thus allowing pseudo-Fano interaction.<sup>10</sup> Inspection of the  $\nu_{4c}$  mode configuration shown in Fig. 1 indicates this mode is indeed expected to become preferentially destabilized by intersite relaxational proton motions. The results of the present experiment clearly show this is just what happens: with the onset of intersite proton motions upon heating in the FE phase, the main  $\nu_{4c}$  mode is destabilized and softens. It couples with lower-frequency modes, mainly with the most intense among them. At the approach of  $T_C$ , the  $\nu_4$  vibrational mode appears split into two components. (i) the upper *underdamped* component corresponds to the part of the response still having the character of a discrete state and, therefore, submitted to the rule of anticrossing. Its downshift is blocked by the immediately lower-LO mode. (ii) The lower component is treated as an *overdamped* mode for the sake of simplicity, thus keeping a description shown to be valid at other temperatures and pressures.<sup>4</sup> It possesses, in fact, a sufficiently marked character of spectral distribution (likely due to the random character of protonic motions that destabilize the  $\nu_{4c}$  mode), rather than discrete state, and gives rise to interference with the neighbor modes in the Fano sense rather than mode-mode coupling. This interference with the main external mode is strong enough to create a new complex pole (near  $80\text{ cm}^{-1}$ ) in the inverse dielectric function that appears simultaneously with the lowest-frequency overdamped TO response. (The real part of the dielectric function is negative in this region at any temperature above 120 K.) The vibrational motion that triggers the phase transition is, therefore, mainly of the  $\nu_{4c}$  type. The Rb ions are also involved in the phase transition

since the main external mode is coupled with the  $\nu_{4c}$  mode.

To test that a soft-mode or a Debye-mode linewidth follows a Curie-Weiss law, as discussed in Brillouin studies (see Ref. 11 and references therein), does not prove that the soft mode triggers the phase transition, because it could be coupled to still lower-frequency unobserved excitation and thus enhance its contribution to the dielectric constant  $\epsilon_0$ .<sup>12</sup> The contribution of the soft mode to  $\epsilon_0$  can be evaluated only when *all* TO-LO splits are known. Infrared reflectivity spectroscopy yields the TO-mode strengths, which are their contribution to the dielectric constant, and this is the decisive advantage. Their sum displayed in the inserts of Fig. 4—effectively, the oscillator strength of the soft mode alone, near  $T_C$  and above—does explain the temperature dependence of the dielectric constant, at least when it is measured in the clamped configuration (above piezoelectric resonances), or under high-bias electric field to ensure a single-domain sample.<sup>13,14</sup>

Summarizing, among the coupled TO modes that show softening upon approaching  $T_C$  (Fig. 4), the  $B_2-\nu_{4c}$  mode first starts softening around 80 K. Its eigenvectors (Fig. 1) are compatible (i) with strong coupling with proton-relaxational motions in the plane perpendicular to the FE axis, and (ii) with the generally accepted configuration of polarization fluctuations along the FE axis. Finally, the most important point is that the temperature dependence of the sum of the oscillator strengths of the  $\nu_{4c}$  external coupled modes amounts to that of the dielectric constant. All this strongly suggests a displacive mechanism. However, the origin of the mode softening is a strong coupling with random protonic motions which is an order-disorder phenomenon.

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