

## Raman spectra of DRADP-50 dipolar glass

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1995 J. Phys.: Condens. Matter 7 683

(<http://iopscience.iop.org/0953-8984/7/3/022>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.179

The article was downloaded on 13/05/2010 at 11:47

Please note that [terms and conditions apply](#).

## Raman spectra of DRADP-50 dipolar glass

Yu I Yuzyuk†, I Gregora, V Vorlíček, J Pokorný and J Petzelt

Institute of Physics, Czech Academy of Sciences, Na Slovance 2, 180 40 Prague 8, Czech Republic

Received 9 August 1994, in final form 17 October 1994

**Abstract.** Raman spectra of an  $\text{Rb}_{0.5}(\text{ND}_4)_{0.5}\text{D}_2\text{PO}_4$  (DRADP-50) mixed crystal have been carefully investigated in the 15–300 K temperature range for all fundamental polarization geometries. The spectra have been interpreted in terms of vibrational modes of principal structural units and critically discussed in comparison with published data on analogous (deuterated and protonated) compounds. Analysis of the temperature dependence of peak positions and halfwidths has made it possible to estimate two characteristic temperature regions ( $\sim 200$ – $220$  K and  $\sim 100$ – $120$  K) where incipient cluster formation and freezing of individual structural units takes place in this compound on cooling through the dipolar glass transition.

### 1. Introduction

$\text{Rb}_{1-x}(\text{NH}_4)_x\text{H}_2\text{PO}_4$  (RADP) and  $\text{Rb}_{1-x}(\text{ND}_4)_x\text{D}_2\text{PO}_4$  (DRADP) mixed crystals form dipolar glasses in a large intermediate concentration range  $0.3 \leq x \leq 0.7$ . These compounds have been extensively studied by different experimental methods: neutron scattering (Grimm *et al* 1986), x-ray diffraction (Courtens *et al* 1984), NMR (Korner *et al* 1993, 1994, Blinc *et al* 1988), dielectric response (Courtens 1986, He 1991).

IR and Raman spectra rank among the most useful methods to investigate the freezing of local distortions in the glass state as they provide information about the symmetry displayed in the lattice locally and momentarily on a nanometric and picosecond scale (averaged over a few interatomic distances and a few atomic vibrational periods only). IR spectra in the compounds of the  $\text{KH}_2\text{PO}_4$  (KDP) type have been recently reviewed by Simon (1992). The first Raman data on powdered RADP-35 have shown that H bonds are not much modified with respect to those of pure crystals down to 20 K. The bands associated with vibrations of  $\text{NH}_4^+$  ions also remain broad at low temperatures, indicating a frozen-in  $\text{NH}_4^+$  orientational disorder in the solid solution (Le Calve *et al* 1989).

In the first Raman study of RADP-35 and RADP-66 crystals it was shown that transformation to glass affects the proton collective modes. Leakage of numerous internal vibration bands into scattering geometries where the bands are not allowed was observed. The important role played by  $\text{NH}_4^+$  fixation to its O neighbours is emphasized by a peculiar temperature dependence of the  $\text{NH}_4^+$  librational mode (Courtens and Vogt 1985). Raman spectra of a 71.4% deuterated crystal DRADP-52 were studied down to 5 K (Martinez *et al* 1987). Special attention was paid to the temperature dependence of the  $\nu_2$  symmetric deformation mode of  $\text{PO}_4$  and of the librational mode of the  $\text{NH}_4^+$  group; assignment of the peaks observed in the Raman spectra was also proposed.

† On leave from the Institute of Physics, Rostov State University, Stachki 194, Rostov-on-Don, 344104, Russia.

The present contribution reports a Raman study of a completely deuterated crystal of DRADP-50. Our Raman spectra at room temperature and, in particular, their temperature dependences are different from the first study (Martinez *et al* 1987). Temperature dependences for four scattering geometries corresponding to different symmetry modes in DRADP-50 have been studied in a wide temperature range down to 20 K and their detailed interpretation is presented. Particular attention is paid to anomalies connected with the formation and freezing of clusters.

## 2. Background

RADP- $x$  and DRADP- $x$  mixed crystals in the concentration range  $0.3 \leq x \leq 0.7$  have tetragonal symmetry (space group  $I\bar{4}2d-D_{2d}^{12}$ ) of the KDP type down to liquid-He temperatures. The factor-group analysis of normal vibrations for such a tetragonal structure where both  $PO_4$  and  $NH_4$  tetrahedra occupy sites of  $S_4$  local symmetry is well known (see, for example, Courtens and Vogt 1985, Simon 1992). However, detailed investigations of the Raman spectra of KDP (Tominaga 1983) showed that the local and momentary site symmetry of  $PO_4$  tetrahedra above  $T_c$  is  $C_2$ , which is the same symmetry as that below  $T_c$ , whereas the  $S_4$  sites correspond to average positions of the  $PO_4$  tetrahedra in the paraelectric phase. Investigations of the Raman spectra of pure crystals of  $NH_4H_2PO_4$  (ADP) and  $ND_4D_2PO_4$  (DADP) at room temperature also show that the  $H_2PO_4^-$  ( $D_2PO_4^-$ ) and  $NH_4^+$  ( $ND_4^+$ ) ions possess  $C_2$  local symmetry (Kasahara *et al* 1986). A Raman study of RADP- $x$  mixed crystals (Courtens and Vogt 1985) confirms dynamical violation of the local symmetry of  $NH_4$  and  $PO_4$  tetrahedra (i.e. dynamical cluster formation), compared to that of the ideal tetragonal structure, even at room temperature; this is manifested by the appearance of lines forbidden by the relevant Raman selection rules. In the glass state the violations are more pronounced and lead to splitting of some lines and stronger depolarization of the Raman spectra.

Isomorphic substitution of the ions with close values of ionic radii,  $NH_4^+$  (1.42 Å)  $\rightarrow$   $Rb^+$  (1.48 Å), leads to marked perturbations of the local symmetry of both  $NH_4$  and  $PO_4$  sublattices in mixed crystals, since each  $NH_4^+$  ion is bound via asymmetric N-H...O bonds with the O in  $PO_4$  groups, which in turn participate in forming the O-H...O bonds (Courtens 1987). This induces distortions of the  $NH_4$  tetrahedron and its shift away from the  $S_4$  site centre, so that the real local symmetry has to be lower: i.e.  $C_2$  or  $C_1$ . Such off-centre location of  $NH_4$  leads to a distortion of the  $PO_4$  group, which should also be manifested in vibrational spectra of the mixed crystals. Moreover, the deuterated crystals DRADP-50, the selection rules in Raman spectra are even more strongly violated: there is a stronger leakage of symmetry-forbidden modes and the internal modes of the  $PO_4$  and  $ND_4$  tetrahedra show larger splittings. This is evidently due to increased distortion of tetrahedral ions on deuteration; in fact, neutron-diffraction studies give evidence for geometric elongation of the H bonds on deuteration (Nelmes 1987).

Analysing the Raman spectra of DRADP-50 on the well known factor-group basis, one can separate the 'main peaks', allowed by selection rules in the  $S_4$  symmetry, from the forbidden lines leaking into other polarization geometries as a result of local symmetry violation. Such an approach has been used by Courtens and Vogt (1985) and appears to be the most useful one. A detailed analysis of the Raman spectra of the DRADP-50 mixed crystal is possible on the basis of preliminary analyses of the spectra of pure crystals of ADP and DADP (Kasahara *et al* 1986),  $RbH_2PO_4$  (RDP) and  $RbD_2PO_4$  (DRDP) (Martinez and Calleja 1985, Mavrin *et al* 1973), mixed crystals of RADP- $x$  with  $x = 35$  and 65 (Courtens and Vogt 1985), and partially deuterated (71.4%) DRADP-52 crystals (Martinez *et al* 1987).

### 3. Experimental details

Raman spectra of DRADP-50 have been measured on a sample in the form of a carefully oriented and optically polished rectangular parallelepiped  $4 \times 3 \times 1 \text{ mm}^3$  (the largest face was perpendicular to the  $z \equiv c$  crystallographic axis) in the right-angle scattering geometry. The sample was placed in a continuous-flow liquid-He optical cryostat (cooling by convection) permitting us to achieve very good temperature stability in the 15–300 K range. The 488 nm line of an  $\text{Ar}^+$  laser was chosen for excitation and the scattered light, collected by a photographic lens, was analysed using a PC-controlled SPEX-14018 double spectrometer equipped with standard photon-counting detection. Special care was taken to ensure identical conditions for all scattering geometries, which were realized by alternatively rotating the polarization of the incident beam and/or the analyser for different sample orientations while keeping the laser power, slit width, and height constant. The spectral slit width was  $\sim 2.5 \text{ cm}^{-1}$ .

### 4. Results and discussion

The Raman spectra of DRADP-50 at 300 K and at 15 K for different scattering geometries are shown in figures 1 and 2, respectively; the corresponding frequencies are summarized in table 1.

In the following discussion the spectral features are grouped according to the underlying individual structural units.

#### 4.1. Raman spectra at room temperature

**4.1.1. Internal modes of  $\text{PO}_4$ .** In accordance with the standard factor-group analysis of the ideal tetragonal KDP structure, the fully symmetric stretching vibration  $\nu_1(\text{A})$  of the  $\text{PO}_4$  ion (labelled  $\nu_1^{\text{P}}$ ) should be observed only in the  $\text{A}_1\text{-y}(\text{zz})\text{x}$  geometry. The frequency of this mode in a free ion is  $980 \text{ cm}^{-1}$  (Herzberg 1966). In DRADP-50 this mode has a frequency of  $882 \text{ cm}^{-1}$ , coinciding with the frequency of an analogous mode in DADP (Kasahara *et al* 1986). In DRDP the  $\nu_1^{\text{P}}$  frequency is close to  $889 \text{ cm}^{-1}$  (Martinez and Calleja 1985). As in RADP- $x$  (Courtens and Vogt 1985), this mode in DRADP-50 is observed also in other geometries, corresponding to the  $\text{B}_2$  and E modes. Its intensity in the  $\text{B}_2$  (LO+TO) spectrum attains  $\sim 10\%$  of that in the  $\text{A}_1$  spectrum; this is a very large value pointing to a lower local symmetry of  $\text{PO}_4$  ions, obviously of dynamic origin. The leakage of the  $\nu_1^{\text{P}}$  mode into the geometry corresponding to E modes is possible only if the  $\text{PO}_4$  ions have  $\text{C}_1$  local symmetry. The intensity of the  $\nu_1$  mode leaking into the E spectra is lower than 5%, which does not permit us to make any definite conclusions.

The doubly degenerate bending mode  $\nu_2^{\text{P}}$  (free-ion value  $363 \text{ cm}^{-1}$ ) should be observed in  $\text{A}_1$ ,  $\text{B}_1$ , and  $\text{B}_2$  Raman spectra provided the  $\text{PO}_4$  ion has  $\text{S}_4$  local symmetry. In DRADP-50 these main lines are observed with the frequencies  $352 \text{ cm}^{-1}$  ( $\text{A}_1$ ) and  $382 \text{ cm}^{-1}$  ( $\text{B}_2$ ). The frequencies of the corresponding lines in pure crystals have very close values:  $346 \text{ cm}^{-1}$  (DADP) and  $355 \text{ cm}^{-1}$  (DRDP) in the  $\text{A}_1$  spectrum, and  $386 \text{ cm}^{-1}$  (DADP) and  $383 \text{ cm}^{-1}$  (DRDP) in the  $\text{B}_2$  spectrum (Kasahara *et al* 1986, Martinez and Calleja 1985, Mavrin *et al* 1973). In DRADP-50, as in RADP- $x$ , the  $\text{B}_2$  and  $\text{A}_1$  components of the  $\nu_2^{\text{P}}$  mode have respectively higher and lower frequencies than the free-ion value, because of their interaction with the H bonds (Courtens and Vogt 1985); deuteration results only in a downshift of both frequencies by several  $\text{cm}^{-1}$ . Note that for  $\nu_2^{\text{P}}$ , in a similar way as for  $\nu_1^{\text{P}}$ , leakage of

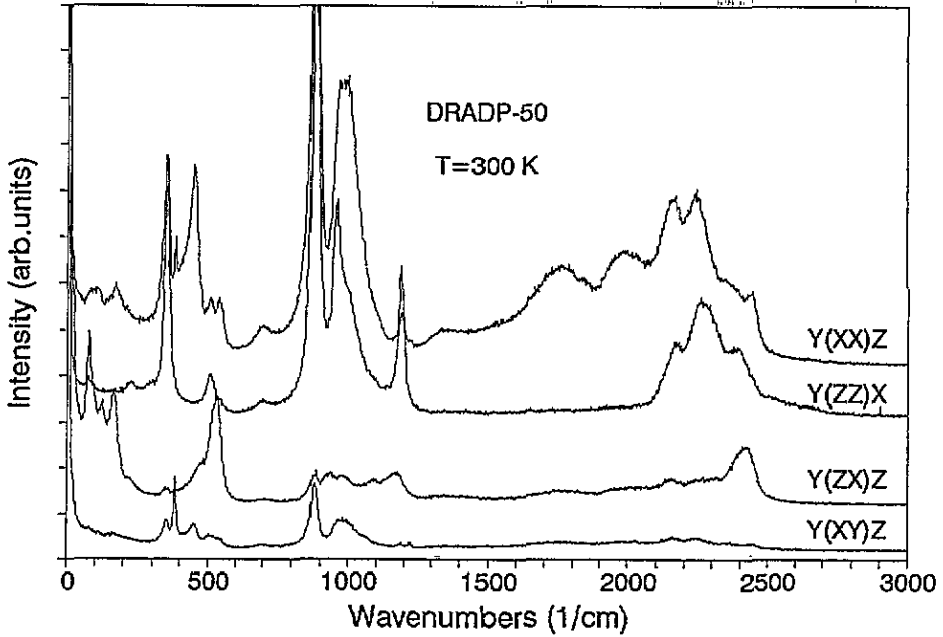


Figure 1. Overall Raman spectra of DRADP-50 at room temperature for four polarization geometries.

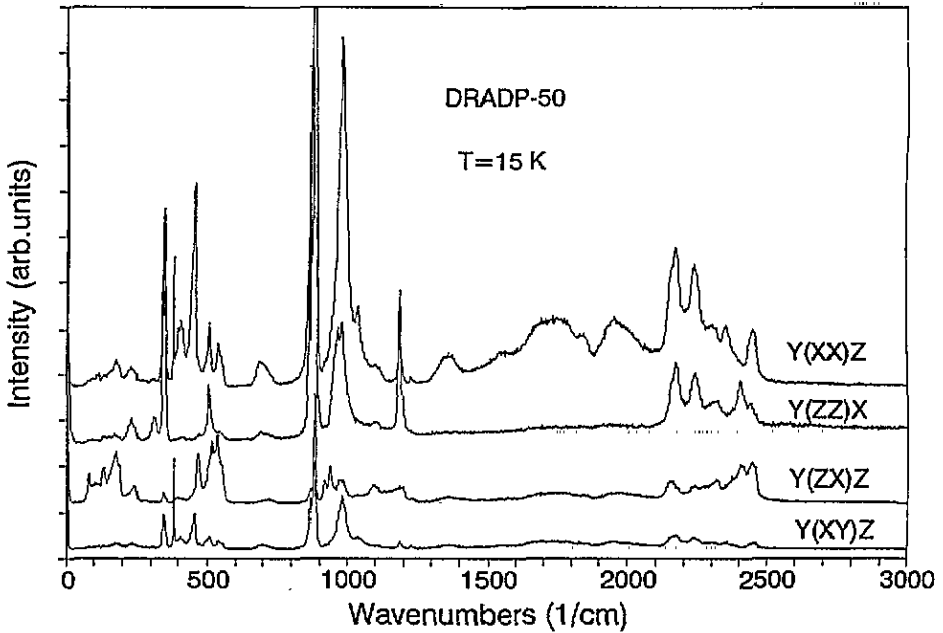


Figure 2. Overall Raman spectra of DRADP-50 at 15 K.

an intense band at  $352\text{ cm}^{-1}$  ( $A_1$ ) into geometries corresponding to  $B_2$  and E modes is observed.

**Table 1.** Frequencies (in  $\text{cm}^{-1}$ ) of observed Raman modes in DRADP-50.  $L^P$ ,  $\text{PO}_4$  librations;  $L^N$ ,  $\text{ND}_4$  librations; \*, main peaks for internal vibrations of the  $\text{PO}_4$  group; s, strong; w, weak; vw, very weak; ?, uncertain.

| $y(xz)z = A_1 + B_1$ |       | $y(zz)x = A_1$ |       | $y(xz)z = E$ |       | $y(xy)z = B_2$ |      | Assignment               |
|----------------------|-------|----------------|-------|--------------|-------|----------------|------|--------------------------|
| 300 K                | 15 K  | 300 K          | 15 K  | 300 K        | 15 K  | 300 K          | 15 K |                          |
| 80w                  |       | 77vw           |       | 78           | 80    | 78vw           |      | External translations    |
| 112w                 | 114vw |                |       | 124          | 108   | 112vw?         | 114? |                          |
|                      |       |                |       | 166          | 132   |                |      |                          |
|                      |       |                |       |              | 174   |                |      | L                        |
| 172                  | 180   |                |       |              | 186   | 170            | 180  | N                        |
|                      | 234   | 219            | 231   | 223          | 239   |                | 236  | L                        |
|                      | 317   |                | 312   |              |       |                |      | } $\nu_2^P$              |
| 350*                 | 349   | 352*           | 348   | 350          | 350   | 352            | 348  |                          |
| 380                  | 383   |                |       |              | 382vw | 382*           | 382  |                          |
|                      | 408   |                |       |              | 400   |                | 408  |                          |
| 450*                 | 454   |                |       |              | 454   | 450*           | 454  | } $\nu_4^P$              |
|                      |       |                |       | 476*         | 468   |                |      |                          |
| 508                  | 508   | 510            | 506   |              | 505   | 510            | 504  |                          |
|                      |       |                |       |              | 518   |                |      |                          |
| 540                  | 542   |                |       | 530*         | 538   | 542            | 540  | } $\nu_4^P$              |
|                      | 550   |                | 545vw |              | 548   |                | 550  |                          |
| 700vw                | 700   | 700vw          | 706   | 706vw        | 718   | 700vw          | 702  | $\gamma(\text{O-D})$     |
| 882s*                | 868   | 882s*          | 868   | 882w         | 868   | 882w           | 868  | $\nu_1^P$                |
|                      | 882s  |                | 882s  |              | 882   |                | 882  |                          |
|                      |       |                |       |              | 918   |                |      | } $\nu_3^P$              |
|                      |       |                |       | 932*         | 938   |                |      |                          |
| 968*                 |       | 956            | 964   |              |       |                |      | } $\nu_3^P$              |
| 990                  | 982   | 988            | 981   | 978          | 978   | 980            | 980  |                          |
|                      | 1038  |                |       |              |       | 1050           | 1040 | } $\delta(\text{O-D})$   |
|                      | 1104  |                | 1104  | 1090         | 1096  |                | 1102 |                          |
| 1188                 | 1186  | 1186           | 1186  | 1168         | 1186  | 1188w          | 1186 | } $\nu_4^N$              |
|                      |       |                |       |              |       | 1120w          | 1228 |                          |
| 1360                 | 1362  |                |       |              |       |                |      | } $\nu_2^N$              |
|                      |       |                |       |              |       |                |      |                          |
|                      | 1560  |                |       |              |       |                |      | } $2\gamma(\text{O-D})?$ |
| 1760                 | 1733  |                |       | 1760         | 1750  | 1760           | 1730 |                          |
|                      | 1838  |                |       |              |       |                |      | } $\nu(\text{O-D})$      |
| 1990                 | 1968  |                |       | 2000         | 1970  | 2005           | 1954 |                          |
| 2156                 | 2166  | 2168           | 2168  | 2150         | 2150  | 2158           | 2162 | } $\nu_1^N$              |
| 2238                 | 2238  | 2268           | 2238  | 2248         | 2240  | 2240           | 2238 |                          |
|                      | 2300  |                | 2310  | 2306         | 2318  |                | 2300 |                          |
| 2350                 | 2350  |                |       |              |       | 2355           | 2352 |                          |
|                      |       | 2390           | 2404  | 2416         | 2408  |                |      | } $\nu_3^N$              |
| 2434                 | 2448  |                | 2440  |              | 2448  | 2430           | 2448 |                          |

The triply degenerate bending vibration  $\nu_4^P$  (free-ion value  $515 \text{ cm}^{-1}$ ) should have a main component in both the  $B_1$  and  $B_2$  spectra and two components in the E spectrum. It is known (Simon 1992) that this mode, owing to its special character connected with the proton collective motions in the  $c$  plane, is sensitive to the existence of additional H bonds; hence the spectra of pure DADP (Kasahara *et al* 1986) and DRDP (Martinez and Calleja

1985) crystals considerably differ in this frequency range. The bands corresponding to  $\nu_4^P$  in DRADP-50 can be clearly interpreted as superpositions of RADP and DRDP spectra (two-mode behaviour); three lines are observed in the  $B_1$  spectrum: at  $450\text{ cm}^{-1}$  (449 in DRDP and 456 in DADP),  $508\text{ cm}^{-1}$  (508 in DRDP), and  $540\text{ cm}^{-1}$  (540 in DADP); the  $B_2$  spectrum contains also three lines:  $450\text{ cm}^{-1}$  (463 in DRDP, 454 in DADP),  $510\text{ cm}^{-1}$  and  $542\text{ cm}^{-1}$  (545 in DRDP); the E modes show a line at  $476\text{ cm}^{-1}$  (from  $460\text{ cm}^{-1}$  in DRDP) and a complex band at  $530\text{ cm}^{-1}$ , which originates from the lines at  $522\text{ cm}^{-1}$  and  $542\text{ cm}^{-1}$  (DADP) and at  $511\text{ cm}^{-1}$  and  $565\text{ cm}^{-1}$ † (DRDP). A splitting of this complex band can be expected at low temperatures.

The region of asymmetric stretching  $\nu_3^P$  ( $1080\text{ cm}^{-1}$  in the free ion) is the most difficult to interpret. In non-deuterated ADP, RDP, and KDP crystals the lines corresponding to  $\nu_3$  at room temperature form a high-frequency wing of the neighbouring intense fully symmetric  $\nu_1^P$  mode, and the frequencies of asymmetric vibrations are not well defined. In deuterated crystals the  $\nu_1^P$  frequency shifts down by about  $40\text{ cm}^{-1}$  and in DADP (as well as in DRDP) there are lines in the  $955\text{--}970\text{ cm}^{-1}$  range (Kasahara *et al* 1986). The intensity of the lines in this frequency range markedly increases with deuteration, obviously owing to a Fermi resonance of the  $\nu_3^P$  modes with the in-plane  $\delta(\text{O-D})$  bending mode; besides, the  $\nu_4$  mode of the  $\text{ND}_4$  ion (labelled  $\nu_4^N$ ) in DADP appears also in this frequency range—its free-ion value being  $1065\text{ cm}^{-1}$  (Nakamoto 1986). This resonance interaction leads to a considerable strength increase of the Raman spectra in the  $900\text{--}1100\text{ cm}^{-1}$  frequency range in deuterated crystals; at variance with the non-deuterated case, two or three lines in each geometry are observed in DRADP-50. The low-frequency lines of this group, at  $930\text{--}968\text{ cm}^{-1}$ , are tentatively attributed to  $\nu_3^P$ , the high-frequency lines at  $1050\text{--}1090\text{ cm}^{-1}$  to  $\nu_4^N$ , and the line at  $\sim 990\text{ cm}^{-1}$  to  $\delta(\text{O-D})$ , but the corresponding normal coordinates are mixed together. There is apparently no correlation with the factor-group analysis for the  $S_4$  site symmetry.

*4.1.2. Internal modes of  $\text{ND}_4$ .* The lowest-lying mode,  $\nu_4^N$ , of the  $\text{ND}_4$  internal vibrations has been discussed above. Main lines of the doubly degenerate bending vibration  $\nu_2^N$  (free-ion value  $1215\text{ cm}^{-1}$ ) in DRADP-50 are observed in the  $A_1$  spectrum at a frequency of  $1186\text{ cm}^{-1}$ , in  $A_1+B_1$  at  $1188\text{ cm}^{-1}$ , and in  $B_2$  at  $1200\text{ cm}^{-1}$ . Like the  $\text{PO}_4$  modes, the  $\text{ND}_4$  internal modes show a leakage into other geometries because of a lower 'real' symmetry. Thus, a line at  $1168\text{ cm}^{-1}$  is observed in the E spectrum, and an additional line at  $1188\text{ cm}^{-1}$  in the  $B_2$  spectrum. Raman spectra of DRADP-50 in the range of stretching vibrations  $\nu_1^N$  (free-ion value  $2214\text{ cm}^{-1}$ ) and  $\nu_3^N$  (free-ion value at  $2346\text{ cm}^{-1}$ ) closely resemble those of DADP (Kasahara *et al* 1986). Absolute values of the peak frequencies do not differ by more than 1% ( $\sim 20\text{ cm}^{-1}$ ). The number of lines observed in this frequency range considerably exceeds that 'allowed' by factor-group analysis for the  $S_4$  site symmetry (though the appearance of overtones is not excluded here; the  $\nu_2^N$  and  $\nu_4^N$  modes tend to hybridize).

In DRADP-50, the  $\nu_1^N$  and  $\nu_3^N$  modes are observed in all scattering geometries with comparable intensities of the main and leaking lines, which is possible only for the  $C_1$  local symmetry of the  $\text{ND}_4$  ions. This is evidently due to larger distortions of  $\text{ND}_4$  groups in deuterated crystals (compared to the non-deuterated case) on their shift from central positions.

*4.1.3. O-D vibrations.* The vibrational spectrum of protons (deuterons) in the H bonds in mixed crystals of RADP- $x$  (DRADP- $x$ ) has not yet received sufficient attention, although

† This line was reported at  $548\text{ cm}^{-1}$  by Mavrin *et al* (1973).

lines corresponding to stretching and bending modes of the deuterons were observed in the Raman spectra of DRADP- $x$  by Martinez *et al* (1987). They were, however, not interpreted as O–D vibrations and were omitted from the discussion.

The in-plane bending  $\delta(\text{O–D})$  mode in DRADP-50 has been already assigned to the band at about  $990\text{ cm}^{-1}$ . The second, out-of-plane, bending mode  $\gamma(\text{O–D})$  is located at about  $700\text{ cm}^{-1}$ . At room temperature the spectra of stretching modes of O–D bonds have similar shapes as in KDP-type crystals (see, for example, Kaminow *et al* 1965, Davydov and Chisler 1980), with a dynamic distribution of deuterons between two potential minima on the O–D...O bonds. The O–D stretching band is observed only in  $y(xx)z$  scattering geometry ( $A_1+B_1$  modes) as a doublet at  $1990\text{--}1760\text{ cm}^{-1}$  followed by a weak band at about  $1360\text{ cm}^{-1}$ . Let us note that these frequencies are very close to those of the infrared and Raman data on DKDP (Kaminow *et al* 1965), DRDP (Mavrin *et al* 1973), and DADP (Wiener *et al* 1970) pure crystals. Very weak bands in the  $1760\text{--}2000\text{ cm}^{-1}$  range are observed in off-diagonal orientations, corresponding to  $B_2$  and E modes. These bands are missing from the  $A_1-y(zz)x$  spectrum, which is obviously due to the location of H bonds in the  $xy$  plane (hence negligible modulation of the  $zz$  component of the polarizability tensor).

The observed frequencies agree well with model calculations of a double-well potential for the KDP-type crystals (Lawrence and Robertson 1981), where the frequency in the deuterated case is predicted to lie in the  $1640\text{--}2235\text{ cm}^{-1}$  range. The doublet structure of this band obviously results from the Fermi antiresonance with the spectrum of two-phonon states.

*4.1.4. External vibrations.* Low-frequency Raman spectra of external vibrations of the KDP-type crystals are sufficiently well studied in connection with the ferroelectric (FE) and antiferroelectric (AFE) phase transitions. Raman spectra of external vibrations in RADP- $x$  mixed crystals have been studied in great detail by Courtens and Vogt (1985). In deuterated mixed crystals DRADP- $x$  the  $B_2$  mode assigned to collective proton motions (hopping) has a frequency below  $10\text{ cm}^{-1}$  and was recently studied by FIR and near-millimetre dielectric spectroscopy (Petzelt *et al* 1993). Our Raman spectra in the range of external vibrations are very close to those obtained earlier by Martinez *et al* (1987), who also gave their assignments.

## 4.2. Temperature evolution

The discussion of the temperature dependence of Raman spectra follows in the same order of structural units as that of the room-temperature spectra.

*4.2.1. PO<sub>4</sub>.* On lowering the temperature we observe further increase in the leakage of the modes and decrease of their widths, which indicates a lowering of the anharmonicity of thermal vibrations and a freezing-in of all sublattices in general non-symmetric positions. This trend is quite monotonic, but the singularities observed in the temperature behaviour of some parameters make it possible to define, albeit not very sharply, two temperature regions, namely  $\sim 100\text{--}120\text{ K}$  and  $\sim 200\text{--}220\text{ K}$ .

(i) The fully symmetric stretching vibration  $\nu_1^P$  splits at low temperatures into two components, at  $868$  and  $882\text{ cm}^{-1}$ , as shown in figure 3(a) and (b). This effect can be attributed to the formation of non-equivalent  $\text{PO}_4$  anions having different surroundings at low temperatures because of the random distribution of  $\text{ND}_4^+$  and  $\text{Rb}^+$  cations in the crystal. We can estimate at what temperature this splitting sets on: the results of a two-oscillator fit to the lineshape of  $\nu_1^P$  are shown in figure 4. In the  $100\text{--}200\text{ K}$  range the frequencies of



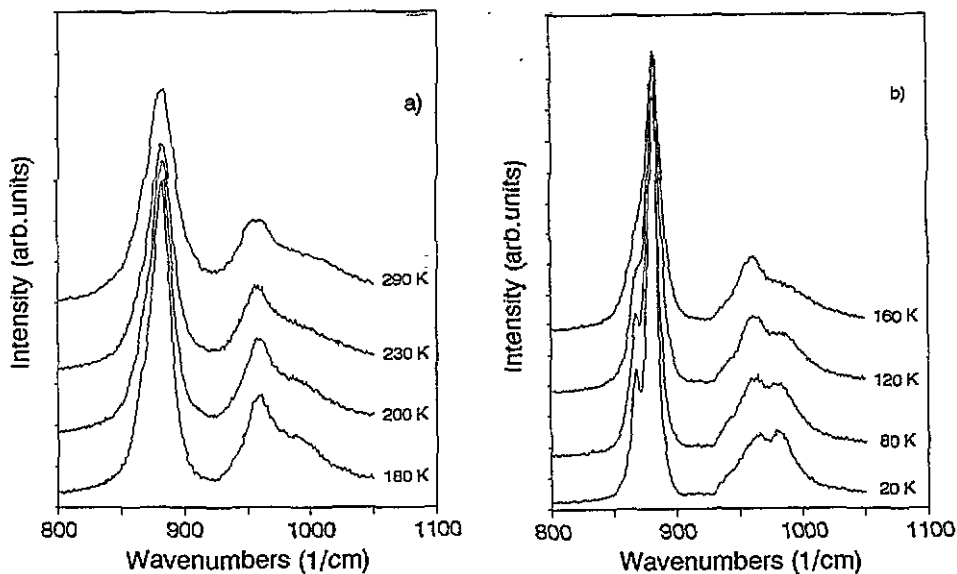


Figure 3. The behaviour of the  $A_1$  component of the symmetric and asymmetric stretching vibration bands  $\nu_1^P$  and  $\nu_3^P$  on cooling.

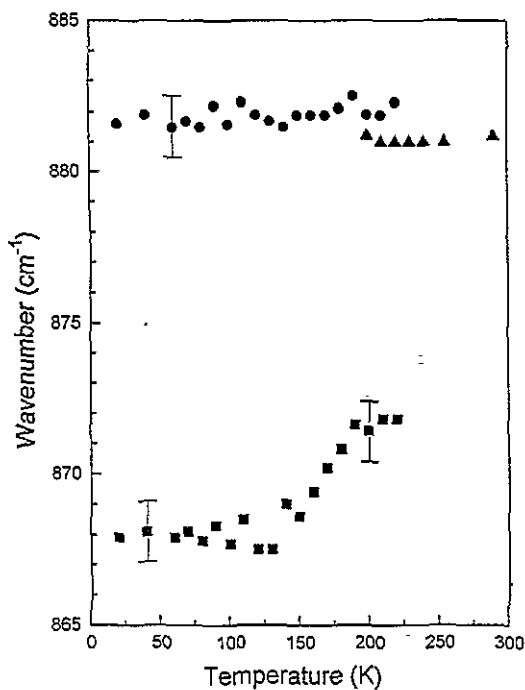


Figure 4. The frequencies of the two components (circles and squares) of the  $\nu_1^P$  band as determined from a two-oscillator fit to the lineshape. Above 200 K the low-frequency component is no longer resolved and a single-oscillator fit (triangles) describes the lineshape equally well.

both components of  $\nu_1^P$  do not vary, but above 120 K the lower-frequency component starts to shift upwards. Both lines eventually merge into one at about 200–220 K and show no further frequency variation between 220 and 300 K.

(ii) Owing to its torsional character, the bending  $\nu_2^P$  mode is sensitive to proton ordering:

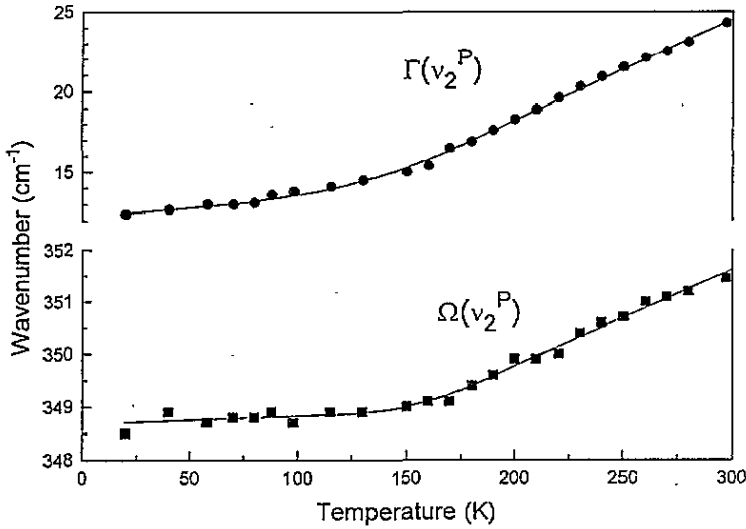


Figure 5. The temperature dependence of the frequency  $\Omega$  (squares) and halfwidth  $\Gamma$  (circles) of the  $v_2^P$  bending vibration, as determined by a Lorentzian fit to the Raman lineshape in the  $A_1$  spectra. Lines are guides for the eye.

in RADP- $x$  Courtens and Vogt (1985) actually observed a lowering of its frequency in the glass state, which is due to the attachment of protons to the  $\text{PO}_4$  anion. The temperature dependence of the frequency and halfwidth of the  $v_2^P$  mode ( $A_1$   $y(zz)x$  geometry) observed by us in DRADP-50 is shown in figure 5; it differs from that found by Martinez *et al* (1987). Both the frequency and halfwidth of this mode show a linear decrease with decreasing temperature in the interval from 300 to  $\sim 150$  K and a change of slope in the 150–120 K range. Below 120 K, however, the width shows only a negligible decrease and the frequency becomes fixed! We explain this behaviour by freezing in of all deuterons below 120 K (see Petzelt *et al* 1993).

(iii) An unusual temperature behaviour is observed in the range of the  $v_3^P$  vibrations. At room temperature there are two lines observed in the  $y(zz)x$  orientation: at  $956\text{ cm}^{-1}$  and at  $\sim 988\text{ cm}^{-1}$  (less resolved peak). On lowering the temperature, the widths of both lines decrease and the high-frequency mode shifts noticeably downwards, until below 120 K a well resolved doublet appears (figure 3(b)). The frequency of the other mode is virtually independent of temperature. If these lines were components of the degenerate  $v_3^P$  mode, we should expect their frequencies to separate with decreasing temperature. However, as noted above, only the line at  $956\text{ cm}^{-1}$  refers to  $v_3^P$  and the broader line at  $\sim 990\text{ cm}^{-1}$  is a bending mode of the O–D...O bond. The latter becomes much narrower on decreasing the temperature from 300 to 100 K, and below 120 K its frequency remains practically constant. This manifests, again, the freezing in of the deuterons.

(iv) The  $v_4^P$  bending mode is evidently connected with proton collective motions and plays an important role in the FE phase transition in RDP (Simon 1992). In DRADP-50, an interesting temperature evolution of the Raman spectra in the corresponding frequency range is observed in the  $y(zx)z$  geometry (E modes), where at room temperature two broad bands at  $476\text{ cm}^{-1}$  and  $530\text{ cm}^{-1}$  appear. On lowering the temperature, the frequency of the  $476\text{ cm}^{-1}$  line drops slightly, but the  $530\text{ cm}^{-1}$  line splits into at least four (!) components—see figure 6. This indicates a lowering of the local site symmetry, apparently due to the formation of  $\text{Rb-PO}_4$  and  $\text{ND}_4\text{-PO}_4$  clusters.

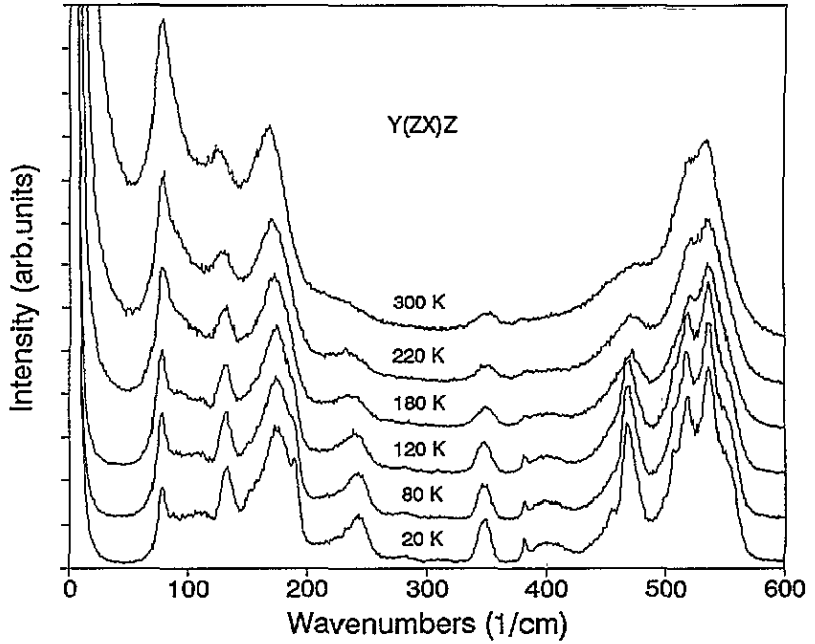


Figure 6. Low-frequency E spectra showing the temperature evolution of the  $\nu_4^p$  and  $\nu_2^p$  bending modes, and of the external modes.

4.2.2.  $ND_4$ . Internal  $ND_4$  modes become narrower with decreasing temperature, most conspicuously between 300 and 200 K, splitting eventually into a large number of components at low temperatures (figure 7). This points undoubtedly to a low  $C_1$  local symmetry of the  $ND_4$  ions in the glass state.

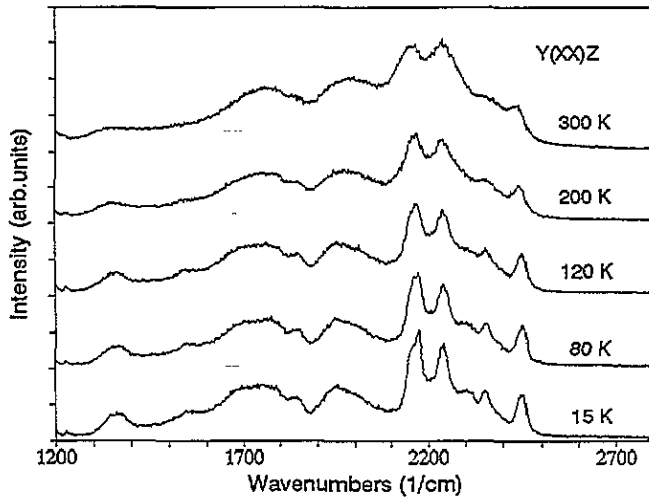


Figure 7. The temperature behaviour of the internal  $ND_4$  modes and  $\nu(O-D)$  modes observed in the  $A_1+B_1$  spectrum.

4.2.3. *OD*. The frequencies of the  $\nu(\text{O-D})$  stretching modes remain practically unchanged in the whole range of temperatures, implying that the bond lengths do not vary with temperature. It is important that the bands due to stretching vibrations remain broad even at 20 K. In pure crystals of KDP, DKDP, and RDP there are also no significant temperature variations of the corresponding band frequencies, but their halfwidths always decrease with decreasing temperature.

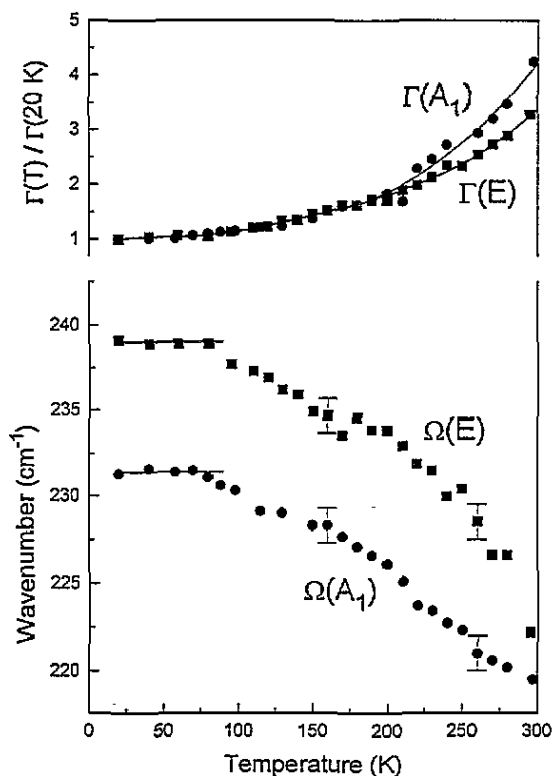


Figure 8. The temperature dependence of the frequencies  $\Omega$  and relative halfwidths  $\Gamma$  of the  $\text{ND}_4$  libration mode in the  $A_1$  (circles) and E (squares) spectra. Lines are guides for the eye.

The potential (double well) for protons is defined by the O atoms. Hence, anharmonic O vibrations and, possibly, reorientations of  $\text{PO}_4$  groups at room temperature lead to a smearing out of this potential. On ordering into FE or AFE phases in pure crystals this smearing diminishes. This does not take place in glass, where both H and O atoms freeze in disordered positions, so the average potential shows a broad distribution.

4.2.4. *External modes*. The most interesting behaviour in the mixed crystals of DRADP-*x* is exhibited by the  $\text{ND}_4$  libration mode, whose anomalous narrowing is due to freezing of  $\text{ND}_4$  groups on glass formation (Courten and Vogt 1985, Martinez *et al* 1987). We have investigated in detail the temperature dependence of this mode for two geometries, corresponding to the  $A_1$  and E symmetries. Temperature dependences of the frequencies and halfwidths are shown in figure 8. The integrated intensity of this line shows no appreciable variation within the whole temperature interval, so the increase in peak values is due to decreasing halfwidth. A considerable decrease in the halfwidth (by a factor of three to four) and the increase of the frequency of the libration mode, in both  $A_1$  and E orientation, indicate that the anharmonicity of these modes decreases and the strength of the bonds to O atoms of the  $\text{PO}_4$  groups increases in the temperature interval from 300 K down to 100–80 K. At

still lower temperatures, the parameters of the libration modes do not significantly vary, so that one can conclude that the freezing of the  $\text{NH}_4^+$  ions takes place at about 80–100 K.

Finally, there is the last important fact: in IR and Raman spectra of pure KDP, RDP, and ADP crystals and their deuterated analogues one always observes a large number of very narrow lines in the low-frequency range corresponding to the external modes. In DRADP-50 the majority of lines in this region remain broad (with halfwidths larger than  $20 \text{ cm}^{-1}$ ), which is a manifestation of the violation of the long-range order of the glass state.

## 5. Conclusions

Our results clearly show that the onset of formation of dynamical clusters should be located at  $\sim 200$ – $220$  K, where a splitting of the  $\nu_1^{\text{P}}$  mode appears in our Raman spectra. This is in agreement with the appearance of incommensurate correlations in neutron scattering, which start to develop below 210 K (Xhonneux *et al* 1988). The onset of a broadening of the  $\text{ND}_4^+$  deuteron NMR lineshapes was also observed below 230 K for  $x = 0.44$  (Blinc *et al* 1988). Note that these temperatures lie only slightly below the phase-transition temperatures of the two pure compounds (DRDP and DADP). The dielectric data on DRADP-40 show a deviation from the Curie–Weiss behaviour at somewhat lower temperatures, namely at 160–180 K (Courstens 1987). Nevertheless, it should be pointed out that even small departures from full deuteration can significantly reduce the transition temperature.

On further lowering the temperature the process of cluster formation progresses rapidly because freezing of  $\text{ND}_4$  rotations takes place, as evidenced by the behaviour of their librational modes shown in figure 8. Simultaneously with this process the freezing of acid deuterons takes place too, as indicated both by the behaviour of the  $\text{PO}_4$  internal modes (figures 4 and 5) and by softening of the deuteron mode (Petzelt *et al* 1993). The process is completed at a freezing temperature of about 100 K. This is in accord with the average value over data reported from various experiments, giving 80–120 K, such as the following.

(i) The dynamical quasielastic contribution to the neutron-scattering spectra disappears on cooling below 110 K (Grimm *et al* 1986) and only elastic scattering is observed below 100 K (Grimm and Martinez 1986) within the resolution limit ( $\sim 1 \text{ cm}^{-1}$ ).

(ii) the incommensurate correlations at  $q_{\Sigma}$  develop upon cooling and saturate near 80 K in neutron scattering in DRADP-62 (Xhonneux *et al* 1988).

(iii) A transition in the inhomogeneous NMR lineshape takes place between 130 and 90 K (Korner *et al* 1993).

(iv) The frequency of the soft deuteron mode tends to very low values ( $< 10^{10}$  Hz) as shown by Petzelt *et al* (1993).

(v) The frequencies of the librational modes of  $\text{ND}_4$  groups and the internal modes of  $\text{PO}_4$  groups become temperature independent.

Our results are in general agreement with other data obtained on fully deuterated samples; they enable us to determine more accurately the temperature of incipient cluster formation.

## Acknowledgments

The authors thank M Ehrensperger and R Kind for providing the DRADP-50 crystal. This work was supported by the Czech Grant Agency, and the grant 93-02-15912 of the Russian Foundation of Fundamental Research.

## References

- Blinic R, Dolinsek J, Schmidt V H and Ailion D C 1988 *Europhys. Lett.* **6** 55
- Courtens E 1986 *Phys. Rev. B* **33** 2975
- 1987 *Ferroelectrics* **72** 229
- Courtens E, Rosenbaum T F, Nagler S E and Horn P H 1984 *Phys. Rev. B* **29** 515
- Courtens E and Vogt H 1985 *J. Chim. Phys.* **82** 317
- Davydov V Y and Chisler E V 1980 *Fiz. Tverd. Tela* **22** 1497
- Grimm H and Martinez J 1986 *Z. Phys. B* **64** 13
- Grimm H, Parlinski K, Schweika W, Courtens E and Arend H 1986 *Phys. Rev. B* **33** 4969
- He P 1991 *J. Phys. Soc. Japan* **60** 313–25
- Herzberg G 1966 *Infrared and Raman Spectra of Polyatomic Molecules* (Princeton, NJ: van Nostrand) p 99
- Kaminov I P, Leite R C C and Porto S P S 1965 *J. Phys. Chem. Solids* **26** 2085
- Kasahara M, Tokunaga M and Tatsuzaki I 1986 *J. Phys. Soc. Japan* **55** 367
- Korner N and Kind R 1994 *Phys. Rev. B* **49** 5918
- Korner N, Pfammater Ch and Kind R 1993 *Phys. Rev. Lett.* **70** 1293
- Lawrence M C and Robertson G N 1981 *Ferroelectrics* **34** 179
- Le Calve N, Romain F, Lamage M H and Novak A 1989 *J. Mol. Struct.* **200** 131
- Martinez J L, Agullo-Rueda F and Schmidt V H 1987 *Ferroelectrics* **76** 23
- Martinez J L and Calleja J M 1985 *Ferroelectrics* **65** 43
- Mavrin B N, Sterin Kh E, Bobrov A V, Rashkovich L N and Mishchenko A V 1973 *Sov. Phys.—Solid State* **15** 1129
- Nakamoto K 1986 *Infrared and Raman Spectra of Inorganic and Coordination Compounds* (New York: Wiley)
- Nelmes R J 1987 *Ferroelectrics* **71** 87
- Petzelt J, Kamba S, Sinitski A V, Pimenov A G, Volkov A A, Kozlov G V and Kind R 1993 *J. Phys.: Condens. Matter* **5** 3573
- Simon P 1992 *Ferroelectrics* **135** 169
- Tominaga Y 1983 *Ferroelectrics* **52** 91
- Wiener E, Levin S and Pelah I 1970 *J. Chem. Phys.* **52** 2881, 2891
- Xhonneux P, Courtens E and Grimm H 1988 *Phys. Rev. B* **38** 9331