Far-infrared reflectivity spectroscopy of potassium ammonium dihydrogenphosphate mixed crystals

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Abstract. The temperature dependence of the far-infrared reflectivity spectra of the potassium ammonium dihydrogenphosphate mixed crystal system, $K_{1-x}(NH_4)_x H_2 PO_4$, is reported for three selected ammonium concentrations, $x = 0.01, 0.3$ and 0.97, over a wide temperature range, 7–250 K. A phase transition is observed in mixed crystals for $x = 0.01$ and 0.97. The occurrence of a glassy state in the mixed crystal for $x = 0.3$ is shown by the spectroscopic study: no ferro- or antiferroelectric order appears upon cooling to liquid helium temperature, and the onset of freezing at about 120 K is manifested by the low-frequency dielectric dispersion observed below 10 cm^{-1}.

1. Introduction

Among the dipolar glasses, the ferroelectric–antiferroelectric solid solution $Rb_{1-x}(NH_4)_x H_2 PO_4$, abbreviated as RADP-$x$, is the best and most intensively investigated system, and constitutes a model for the study of the physics of frustrated materials (Courtens 1987). The characteristic feature of the crystals in this system is that they form dipolar glasses in the intermediate concentration range $0.22 < x < 0.74$, while for $x < 0.22$ and $x > 0.74$, the mixed crystals undergo respectively a ferroelectric (FE) and an antiferroelectric (AFE) phase transition (Courtens 1987). The competition between the FE and AFE tendencies of RbH_2PO_4 and $(NH_4)H_2PO_4$, in the intermediate concentration range, leads upon cooling to a low-temperature structure that looks like a disordered glassy distribution of electric dipolar moments. This proton glass system belongs to the best investigated structural glasses, which represent the most intensively studied class of dielectric materials during the last five years. A review of the dynamical properties of the RADP-x system can be found in the article of Courtens (1987). Recently, infrared reflectivity data were published for RADP-0.5 (Petzelt *et al* 1991) and for RADP-0.3 and 0.72 (Simon and Gervais 1992).

The mixed crystal system $K_{1-x}(NH_4)_x H_2 PO_4$, abbreviated as KADP-x, has been established to be analogous to RADP-x, but its phase diagram is not actually known as accurately (Ono *et al* 1987). The vanishing of the FE or AFE phase transition was observed in the concentration range $0.2 < x < 0.85$ (Ono *et al* 1987), and dielectric measurements on KADP-0.23 have shown the glassy low-frequency dispersion of the dielectric constant (Ono *et al* 1988). Structural studies have shown that this latter mixed crystal maintains it paraelectric (PE) tetragonal structure ($I\bar{4}2d$) down to 20 K, with four formula units in the unit cell (Ono and Yamada 1991, Ono *et al* 1991), in

agreement with the results of our infrared reflectivity spectroscopic study on KADP-0.3 (Wyncke *et al* 1990, Vaezzadeh *et al* 1992). Previous to these studies, Choi and Kim (1983) and Kim *et al* (1983) have studied the $(NH_4)H_2PO_4$ (ADP) impurity effects on the dielectric behaviour of KH_2PO_4 (KDP), while the impurity effects of KDP on the AFE phase transition of ADP crystals was studied by Lee *et al* (1985). Raman spectra of a KADP-0.5 powder sample at 300 and 80 K were published by Kim and Sherman (1987).

In the present paper we report the temperature dependence of the polarized infrared reflectivity spectra of KADP-x mixed crystals for several typical values of the concentration x. This work tries to fill the gap in the experimental vibrational studies of the KADP-x system. The results are compared to the infrared reflectivity spectroscopic studies of pure compounds: KDP (Bréhat and Wyncke 1985, Simon and Gervais 1985, Wyncke and Bréhat 1986, Simon *et al* 1988) and ADP (Bréhat *et al* 1986, Simon 1989).

2. Experimental details

The crystals KDP and ADP belong to the tetragonal structure ($I\bar{4}2d$) in their PE phase, and thus mixed crystals of $K_{1-x}(NH_4)_x H_2PO_4$ formula can be grown by slow evaporation of saturated aqueous solutions of mixed pure salts. We have successfully grown single crystals of KADP-x with a wide variety of ammonium concentration x between 0 and 1. The mixed crystals are tetragonal, their habits are similar to those of pure KDP or ADP according to the value of x, and their sizes are at least $15 \times 15 \times 50$ mm³. The ammonium concentration x was determined after the measurement of the lattice constants of the crystals, by using the relationship given by Ono *et al* (1987).

Polarized infrared reflectivity spectra were performed in the frequency range 15–600 cm⁻¹, between 7 and 250 K, using a grating infrared spectrometer. The studied samples were plane plates of (1 0 0) and (0 0 1) orientations, $12 \times 12 \times 6$ mm³ in size, cut from crystals of different concentration, and then polished to optical quality.

3. Infrared reflectivity spectra and their analysis

3.1. Infrared reflectivity spectra

The temperature dependence of the polarized infrared reflectivity spectra, for three selected ammonium concentrations, $x = 0.01, 0.3$ and 0.97, is displayed in figures 1 to 3. The infrared reflectivity spectra were recorded for both polarizations of the electric field, parallel (figures 1(*a*), 2(*a*) and 3(*a*)) and perpendicular (figures 1(*b*), 2(*b*) and 3(*b*)) to the tetragonal *c* axis of the PE structure.

The polarization of the infrared light along the *c* axis of the studied samples, which belong to the tetragonal symmetry ($I\bar{4}2d$) at room temperature, allows the study of the B_2 modes, and the perpendicular polarization, that of the doubly degenerate E modes of the PE phase (Simon *et al* 1988, Simon 1989).

When a FE phase transition occurs in the KDP family of crystals, the a and b axes of the tetragonal structure are rotated by 45° about the *c* axis. In order to study the B_1 and B_2 modes of the orthorhombic FE structure ($Fdd2$), which because of the polydomain structure of the FE phase cannot be observed separately (Wyncke
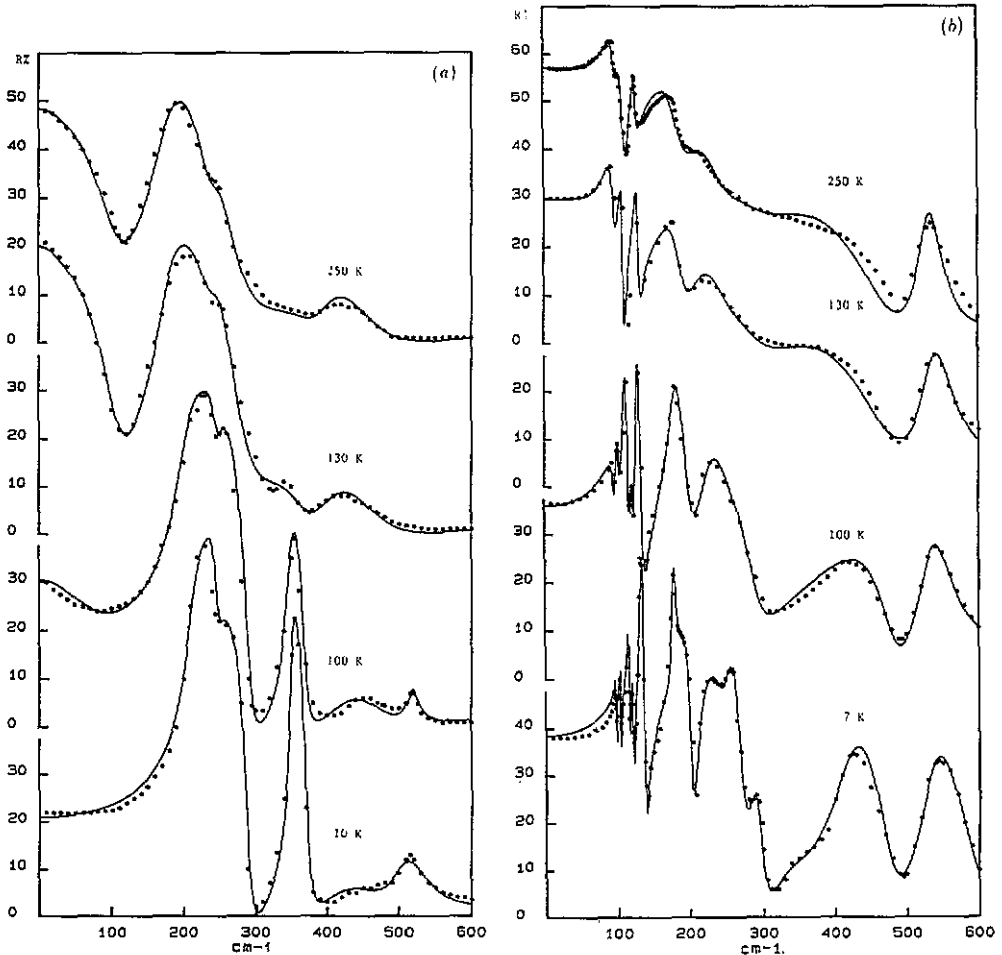
Figure 1. Temperature dependence of the KADP-0.01 reflectivity spectra polarized (*a*) along the *c* axis and (*b*) perpendicular to the *c* axis: full circles, experiment; full curves, best simulation with model equation (1).

and Bréhat 1986), the light was polarized along the [1 1 0] direction of the (0 0 1) tetragonal plate; while for polarization parallel to the *c* axis, the A_1 modes are observed in the FE phase (Bréhat and Wyncke 1985, Simon *et al* 1988).

When an AFE phase transition occurs to the orthorhombic AFE structure ($P2_12_12_1$) as in ADP, the polarization of the infrared light parallel to the *c* axis corresponds to the B_1 modes (Bréhat *et al* 1986, Simon 1989), and the polarization parallel to the *a* or *b* axis, which remain the same as those of the PE phase, allows the study of the B_2 and B_3 modes, which cannot be separated owing to the polydomain structure of the AFE phase (Bréhat *et al* 1986, Simon 1989).

3.2. Dielectric function model

We have used the factorized form of the dielectric function (Simon *et al* 1988) to fit
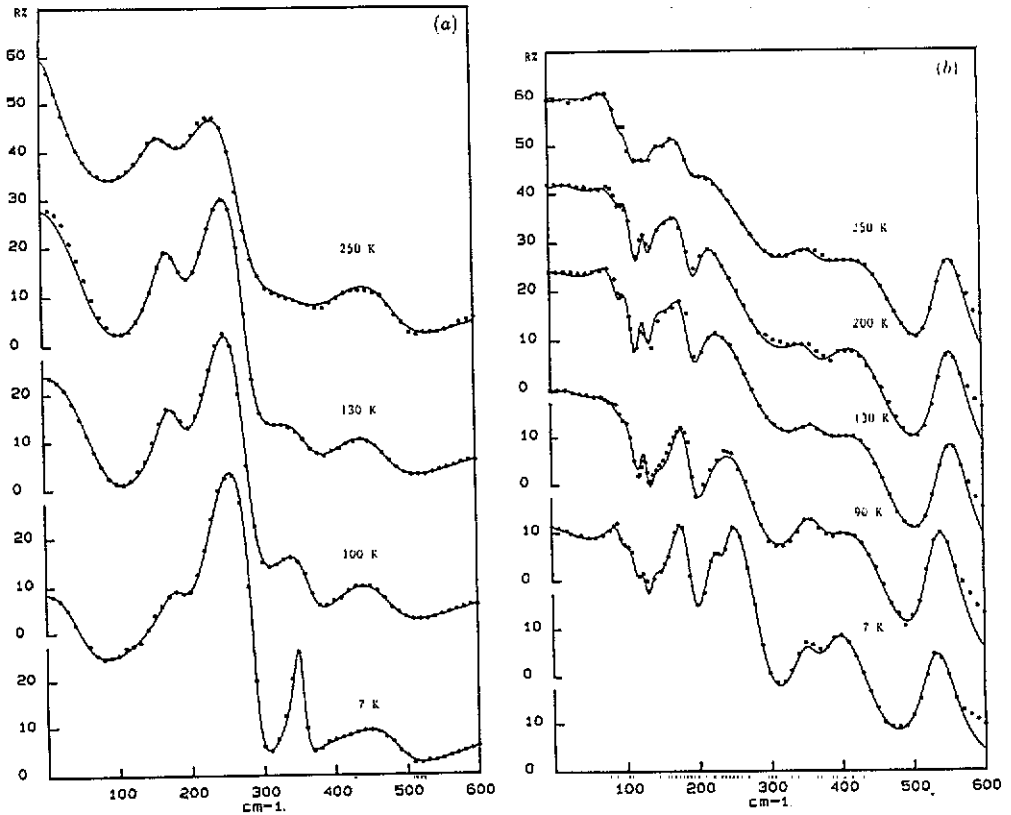
Figure 2. As in figure 1 for KADP-0.3.

the experimental reflectivity spectra:

$$\bar{\epsilon}(\omega) = \epsilon_\infty \prod_j \frac{\Omega_{jLO}^2 - \omega^2 + i\gamma_{jLO}\omega}{\Omega_{jTO}^2 - \omega^2 + i\gamma_{jTO}\omega} \tag{1}$$

This model, which uses only two adjustable parameters, frequency Ω_j and damping γ_j, for each transverse optical (TO) and longitudinal optical (LO) mode, has given satisfactory results in the case of KDP-type pure crystals (Bréhat and Wyncke 1985, Simon *et al* 1988). With this model, good fits were achieved in the present work at each temperature, as shown in figures 1 to 3.

The TO oscillator strength of mode j is calculated from the TO–LO splitting of the optical modes by using the relation (Simon *et al* 1988):

$$\Delta\epsilon_j = \epsilon_\infty \left(\frac{\Omega_{jLO}^2}{\Omega_{jTO}^2} - 1 \right) \prod_{j \neq k} \frac{\Omega_{kLO}^2 - \Omega_{jTO}^2}{\Omega_{kTO}^2 - \Omega_{jTO}^2}. \tag{2}$$

The sum of the TO oscillator strengths is the lattice-mode contribution to the dielectric constant:

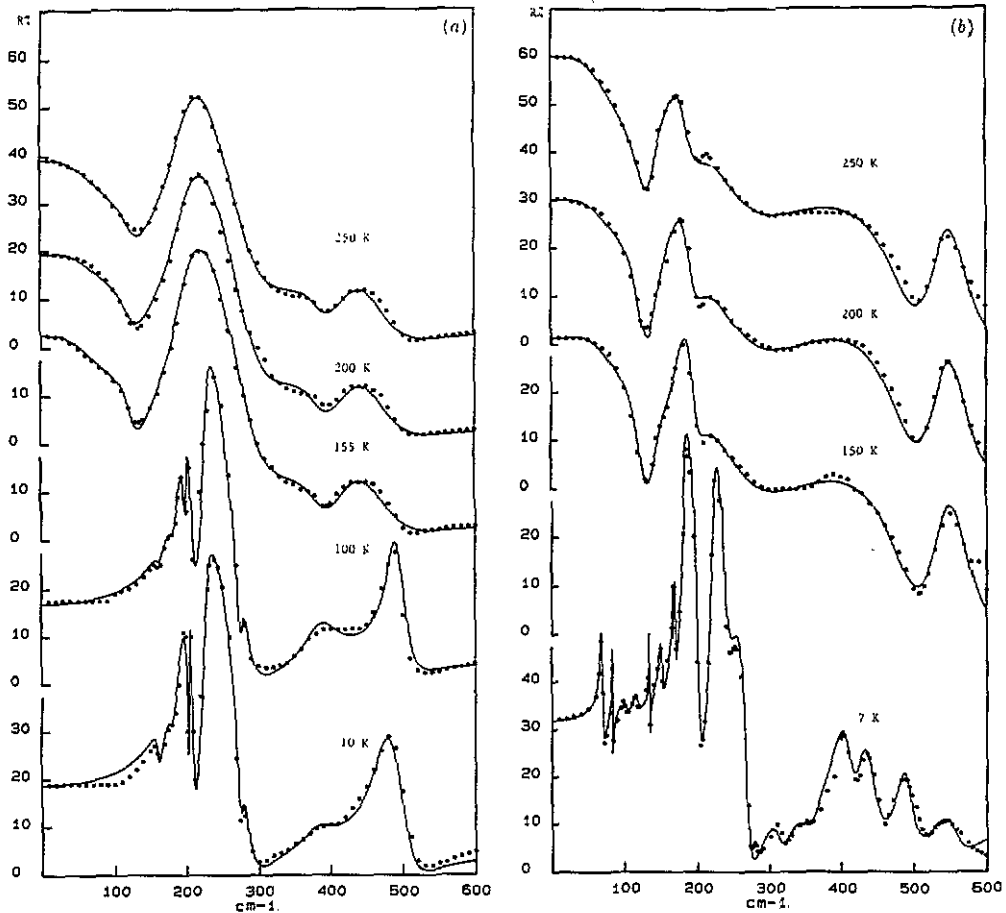$$\epsilon_0 = \epsilon_\infty + \sum_j \Delta\epsilon_j. \tag{3}$$

Figure 3. As in figure 1 for KADP-0.97.

4. Results and discussion

Two types of KADP-x mixed crystals are differentiated from the present infrared reflectivity spectroscopic study: crystals that undergo a FE or AFE phase transition and crystals that did not undergo any phase transition between 300 and 7 K. Another result evidenced by the present study is the double-mode behaviour of the translational lattice mode polarized along the c axis, observed in all studied crystals at 250 K for $0 < x < 1$.

4.1. Phase transitions in mixed crystals of the KADP-x system

From the temperature dependence of the infrared reflectivity spectra between 300 and 7 K, we observed a PE–FE phase transition in the potassium-rich crystals, $x = 0.01, 0.15$, and in a similar way a PE–AFE phase transition in the ammonium-rich crystals, $x = 0.85, 0.97$.

4.1.1. Ferroelectric phase transition.
Typical spectra for KADP-0.01 are shown in figure 1. The temperature dependence of the TO and LO optical mode frequencies lower than

600 cm^{-1}, obtained from the simulation of the experimental data (section 3.2), is displayed in figure 4. These results show that the mixed crystal KADP-0.01 undergoes a PE–FE phase transition at 120 K. This value for $x = 0.01$ is in good agreement with the dielectric measurements of Kim *et al* (1983).

(i) When the electric field is polarized along the c axis, the only difference between the infrared reflectivity spectra of KADP-0.01 (figure 1(*a*)) and those of pure KDP (Bréhat and Wyncke 1985, Simon *et al* 1988) is the small dip observed near 250 cm^{-1} (figure 1(*a*)), which indicates a two-mode behaviour for the translational optical phonon mode (figure 4(*a*)).

In the PE phase, above 120 K, all the modes observed experimentally are symmetry-allowed, apart from the lowest-frequency overdamped mode (figure 4(*a*)). This low-frequency mode disappears 20 K below the phase transition temperature in the FE phase. Its TO oscillator strength calculated from relation (2) constitutes the most important contribution of the optical modes to the static dielectric constant, and explains the variation of the low-frequency reflectivity, as in pure KDP. This is the ferroelectric soft mode of the KDP-type crystals (Bréhat and Wyncke 1985, Simon and Gervais 1985, Simon *et al* 1988).

In the FE phase, below 120 K, the damping of all modes decreases significantly, except that of the ν_{4c} PO$_4$ internal mode observed at 435 cm^{-1} at 100 K (figure 4(*a*)), which remains relatively high even at 10 K ($\gamma = 130$ cm^{-1}). The ν_2 PO$_4$ internal mode at 350 cm^{-1} (figure 4(*a*)) is clearly observed in the FE phase (figure 1(*a*)), but as in pure KDP we did not observe the expected librational mode.

The temperature dependence of the optical modes of KADP-0.01, polarized along the c axis, is quite similar to that of pure KDP. Thus the transition of this mixed crystal is a PE–FE one, induced by the coupling of the ν_{4c} PO$_4$ internal mode to the external translational mode. The frequency of the ν_{4c} PO$_4$ mode, destabilized by the order–disorder intersite proton motion, decreases upon approaching T_c from below. The frequency of the translational mode shifts down at the same temperature, while the overdamped low-frequency mode appears (figure 4(*a*)) (Bréhat and Wyncke 1985, Simon and Gervais 1985, Simon *et al* 1988).

(ii) When the electric field is polarized perpendicular to the c axis in the PE phase, above 120 K, the spectra of KADP-0.01 (figure 1(*b*)) and the temperature dependence of the TO and LO optical mode frequencies (figures 4(*a*) and (*c*)) are quite similar to those of pure KDP (Wyncke and Bréhat 1986). The five expected lattice modes are observed below 300 cm^{-1}, and the two ν_4 PO$_4$ internal modes between 350 and 600 cm^{-1} (figure 4(*a*)).

Figure 1(*b*) displays the reflectivity spectra in the FE phase, for the polarization of the electric field parallel to the [1 1 0] direction of the (0 0 1) tetragonal structure (section 3.1); the temperature dependence of the TO and LO optical mode frequencies is displayed in figures 4(*b*) and (*c*). The observed modes correspond to the B$_1$ and B$_2$ modes, which cannot be separated (section 3.1). These results are quite similar to those of pure KDP (Wyncke and Bréhat 1986).

We have observed that, below 120 K, the reflectivity spectra polarized along the [1 1 0] and [0 1 0] directions of the tetragonal structure are quite identical, but different from those observed along the a and b axes of the FE orthorhombic structure displayed in figures 4(*b*) and (*c*), as previously observed in pure KDP (Wyncke and Bréhat 1991).

(iii) We now consider the dielectric constant in the low-frequency limit. The optical-modes contribution to the static dielectric constant, ϵ_{lat}, calculated through
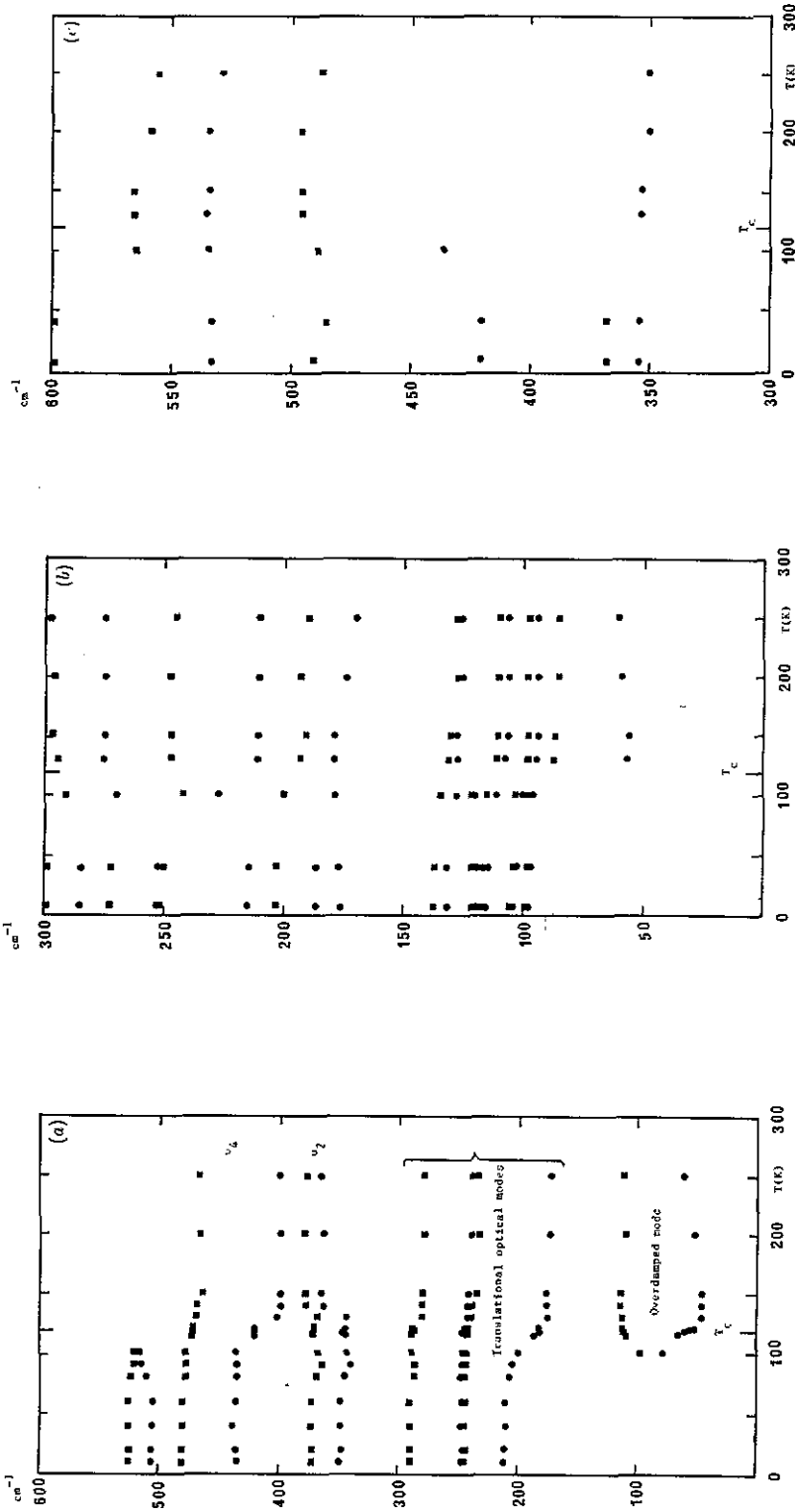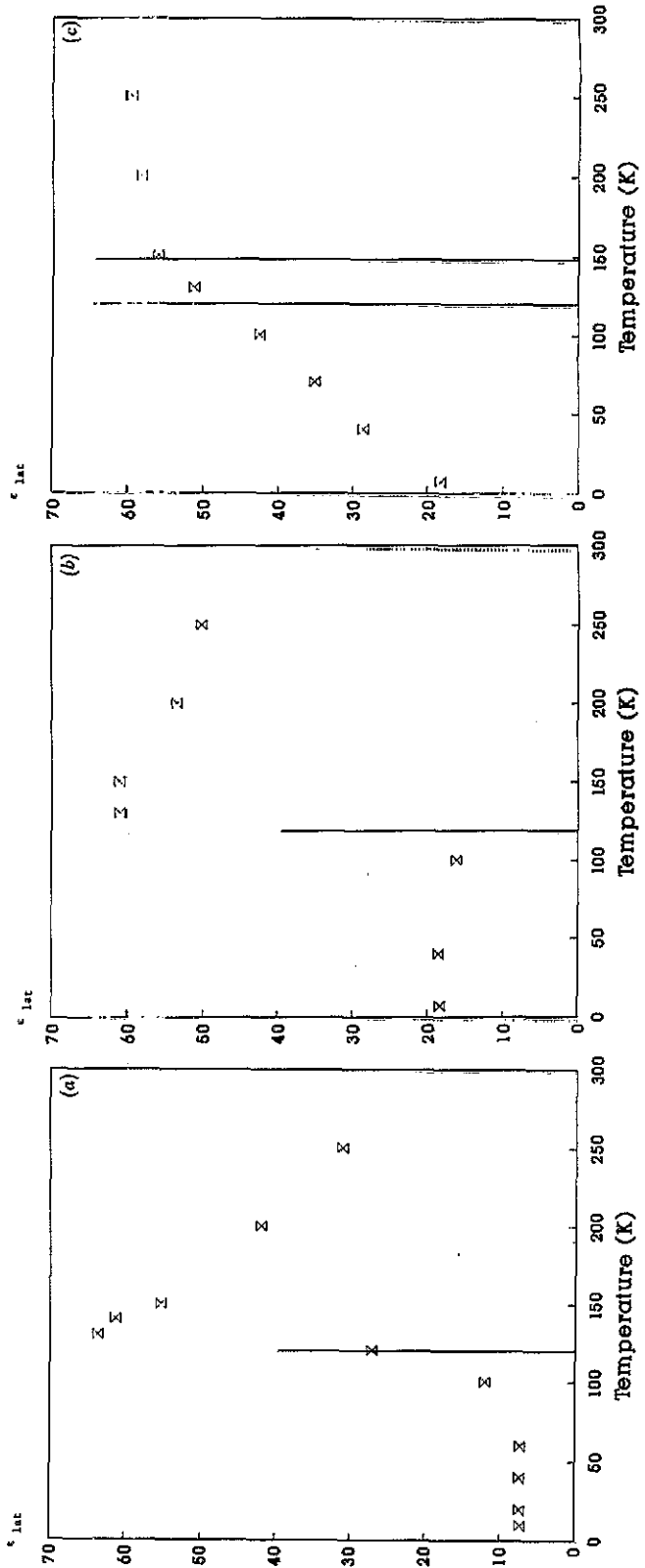
Figure 4. Temperature dependence of the TO (●) and LO (■) optical mode frequencies of KADP-0.01 mixed crystal: (*a*) polarized along the *c* axis; (*b*) and (*c*) polarized perpendicular to the *c* axis, showing (*b*) lattice mode frequencies and (*c*) ν_H suppressed PO_4 internal mode frequencies.
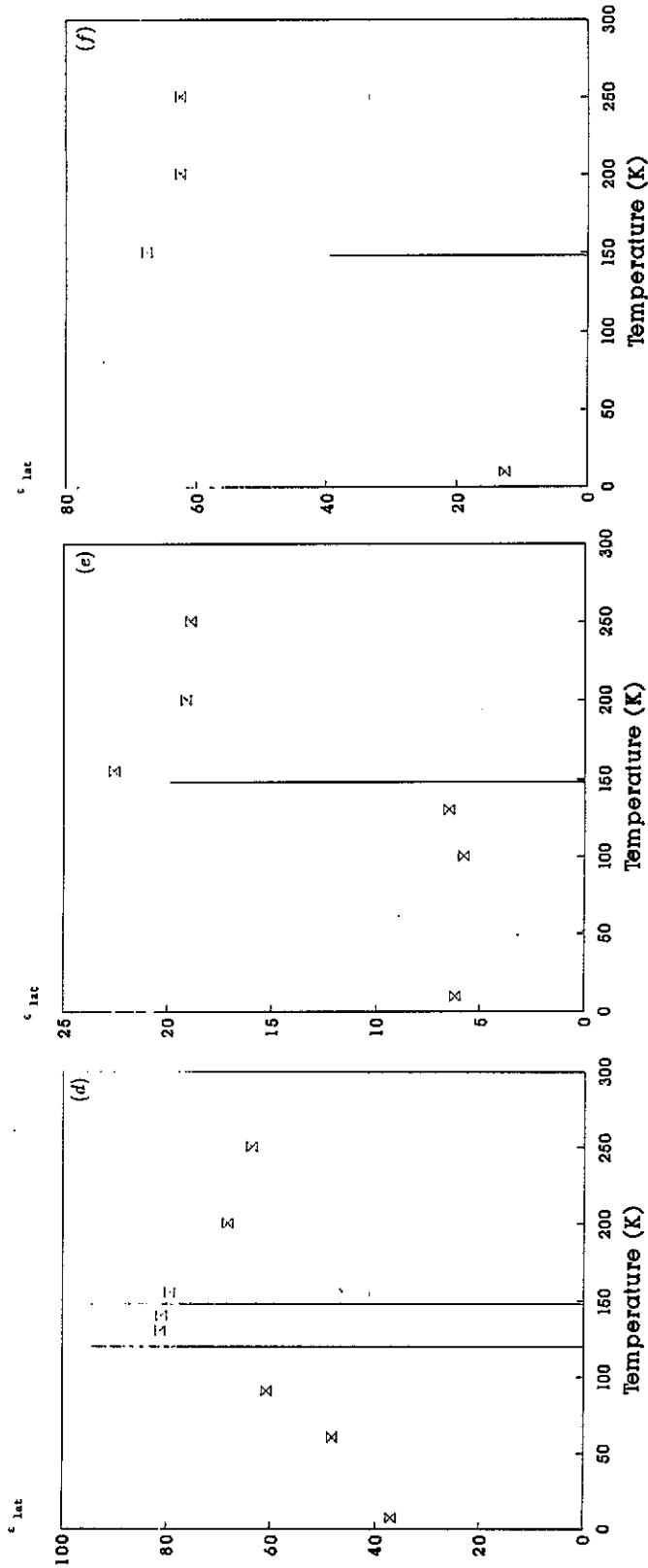
Figure 5. Temperature dependence of ϵ_{lat}, contribution of the optical modes to the the dielectric constant, calculated from the the TO and LO optical frequencies using equation (3), for polarization parallel and perpendicular to the c axis respectively: (*a*) and (*b*) for KADP-0.01; (*c*) and (*d*) for KADP-0.3; (*e*) and (*f*) for KADP-0.97.

relation (3) from the TO and LO frequencies obtained by the simulation, is displayed in figures 5(*a*) and (*b*) respectively for polarization parallel and perpendicular to the *c* axis; ϵ_{lat} allows one to estimate the dielectric constant in the low-frequency limit of the reported spectra (about 10 cm^{-1}). The obtained values of ϵ_{lat} are in good agreement with the measured dielectric constant of pure KDP at 9.2 GHz, for both polarizations (Bréhat and Wyncke 1985, Wyncke and Bréhat 1986). The sharp variation of ϵ_{lat} at 120 K (figures 5(*a*) and (*b*) evidences the PE–FE phase transition of KADP-0.01 mixed crystal. The present results show clearly that KADP-0.01 mixed crystal undergoes a PE–FE phase transition at 120 K, identical to that of pure KDP.

4.1.2. Antiferroelectric phase transition. The temperature dependence of the infrared reflectivity spectra of a KADP-0.97 mixed crystal, displayed in figure 3, is quite similar to that of pure ADP (Bréhat *et al* 1986, Simon 1989). All spectra were simulated with model equation (1); the resulting set of optical mode parameters are reported in figure 6. The transition temperature was determined at 140 K, in agreement with the dielectric measurements of Lee *et al* (1985) for $x = 0.97$. As for pure ADP, the studied crystal shatters at the transition temperature.

(i) In the PE phase, above 140 K, the spectra are practically temperature-independent, even the lowest-frequency heavily damped modes observed in both B$_2$ and E polarizations (figure 6). These two modes, which are the strongest polar ones, are symmetry-forbidden in the PE structure. They suddenly disappear at the phase transition temperature 140 K (figure 6), as in pure ADP (Bréhat *et al* 1986, Simon 1989).

(ii) In the AFE phase, the number of observed modes is much smaller than expected, as in pure ADP (Bréhat *et al* 1986, Simon 1989). The spectra polarized along the *a* and *b* axes of the AFE structure are identical, and correspond to the superposition of the B$_2$ and B$_3$ modes (section 3.1). The only assignments that can be made unambiguously are the small mode at 310 cm^{-1} (figures 3(*b*) and 6(*b*)), which corresponds to the NH$_4$ libration, and the ν_2 and ν_4 internal modes of the PO$_4$ groups observed between 350 and 600 cm^{-1} (figures 3(*b*) and 6(*b*)). The B$_1$ modes are obtained for polarization along the *c* axis (figures 3(*a*) and 6(*a*)) and divided into external and internal vibrational modes.

(iii) The low-frequency dielectric constant ϵ_{lat} calculated from relation (3) is displayed respectively in figures 5(*e*) and 5(*f*) for polarization along the *c* axis and along the *a* axis. For both polarizations, the obtained values are in agreement with the measured dielectric constant of pure ADP at 9.2 GHz (Bréhat *et al* 1986), and also with the measurements of Lee *et al* (1985). The sharp variation of ϵ_{lat} at 140 K (figure 5) evidences the PE–AFE phase transition of KADP-0.97 mixed crystal.

4.2. Vanishing of the phase transition: KADP-x dipolar glasses

Figures 2(*a*) and (*b*) display the temperature dependence of the reflectivity spectra of a KADP-0.3 mixed crystal, respectively for polarization parallel to the *c* axis and to the *a* axis of the tetragonal PE structure. The spectra displayed in figure 2 are in good agreement with those obtained on the RADP-*x* system in the intermediate concentration range $0.22 < x < 0.74$ by Petzelt *et al* (1991) and Simon and Gervais (1992). The temperature dependence of the TO and LO optical mode frequencies obtained from the simulation of the experimental data (section 3.2), displayed in figure 7, shows that except for the two lowest-frequency B$_2$ and E modes, all other mode frequencies are almost temperature-independent. Thus, contrarily to the two
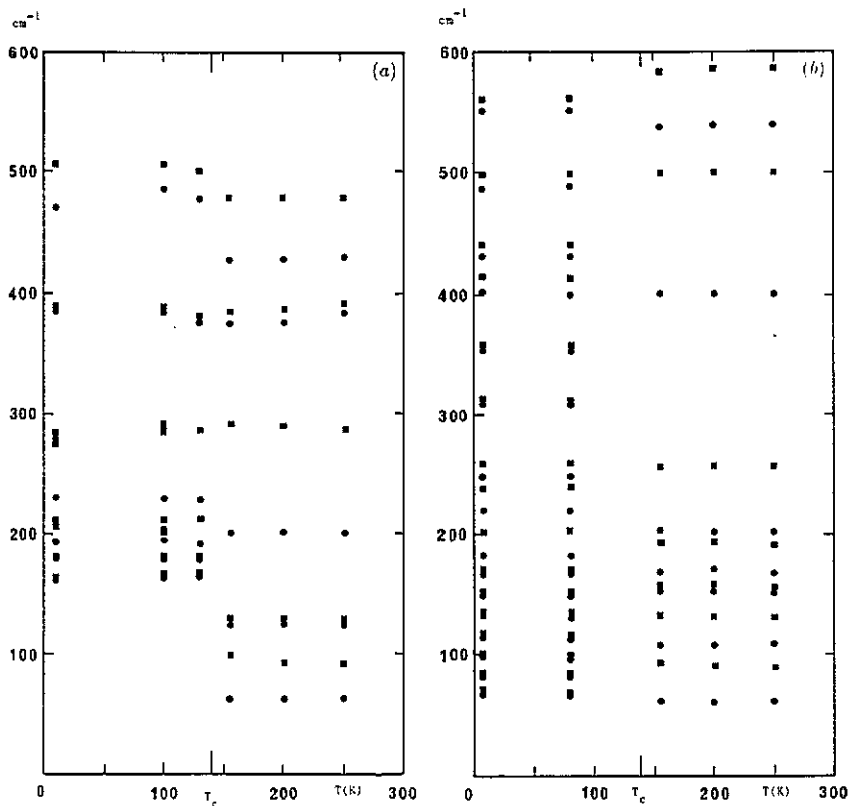
Figure 6. Temperature dependence of the TO (●) and LO (■) optical mode frequencies of KADP-0.97 mixed crystal, polarized (*a*) along the *c* axis and (*b*) perpendicular to the *c* axis.

studied mixed crystals, KADP-0.01 and KADP-0.97 (section 4.1), the KADP-0.3 mixed crystal does not undergo any phase transition between 300 and 7 K. From the results reported in figures 2 and 7, we can conclude that the crystal maintains its PE tetragonal structure down to liquid helium temperature, which was clearly established by the crystallographic studies of Ono and Yamada (1991) and Ono *et al* (1991) on a KADP-0.22 mixed crystal.

The vanishing of the phase transition for the mixed crystals of the intermediate concentration range (Ono *et al* 1987) indicates the occurrence of a glassy state in which the ammonium ions play an essential role in the frustration phenomenon. The crystallographic studies of Ono *et al* (1991) and Ono and Yamada (1991) show that, upon cooling KADP-x crystals of the intermediate concentration range (e.g. $x = 0.22$), NH_4^+ freezing occurs around 120 K, which forces the double minimum potentials of acid protons around the NH_4 groups to asymmetrize. These protons gradually localize at the more stable one of the two sites with decreasing temperature, in such a way that they are attached locally in alternate 'up' and 'down' positions on the PO_4 tetrahedra, which is incompatible with the 'all-up' or 'all-down' Slater configuration of the FE phase (Courtens 1982). Thus in the intermediate concentration range, the competition between acid proton configurations favoured by the freezing of the
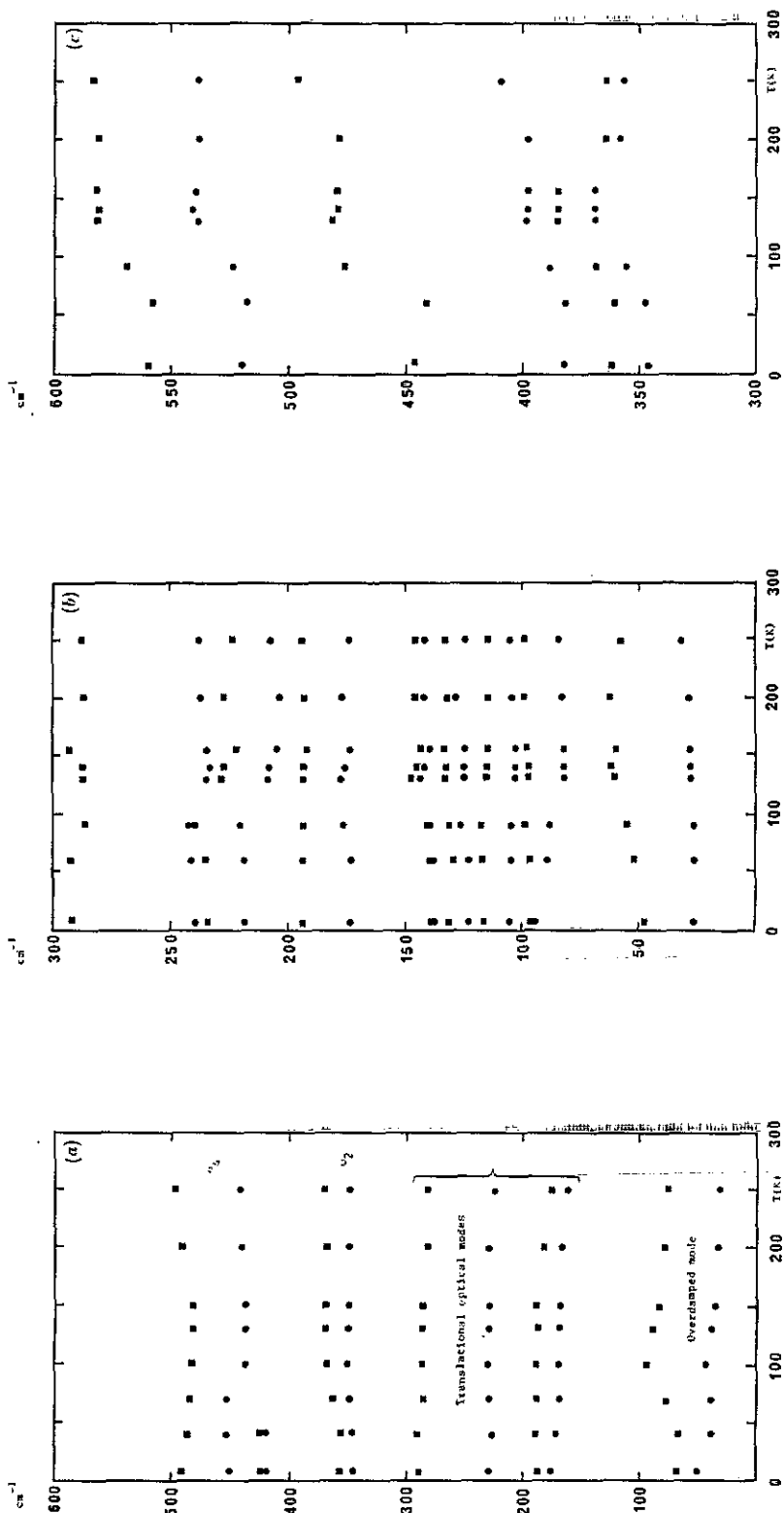
Figure 7. Temperature dependence of the TO (●) and LO (■) optical mode frequencies of KADP-0.3 mixed crystal: (*a*) polarized along the *c* axis; (*b*) and (*c*) polarized perpendicular to the *c* axis, showing (*b*) lattice mode frequencies and (*c*) PO$_4$ internal mode frequencies.

NH_4^+ (AFE order), and the Slater configuration favoured in the pure KDP structure (FE order), leads to the formation of structural glasses; the KADP-x low-temperature structure below 120 K looks like a disordered 'glassy' distribution of electrical dipolar moments.

4.2.1. Electric field polarized along the c axis. The spectra between 300 and 130 K (figure 2(*a*)) are very similar to those of pure KDP and ADP in their PE phase, except that two translational lattice modes are clearly observed at every temperature (figure 2(*a*)), in agreement with infrared reflectivity studies on RADP-x (Petzelt *et al* 1991, Simon and Gervais 1992) and with Raman diffusion (Courtens and Vogt 1985, Lee and Kim 1988).

All modes can be identified without any doubt: the low-frequency highly damped mode, which does not soften between 300 and 7 K, is overdamped ($\gamma/\Omega > 1.4$) even at 7 K; the translational lattice mode, which has a double-mode behaviour; and the ν_2 and ν_4 internal modes of the PO_4 groups (figure 7(*a*)). Upon cooling below 130 K, the TO oscillator strength strength of the lowest-frequency mode and the damping of all modes decrease; particularly the ν_2 internal mode is strongly narrowed (figure 2(*a*)). Apart from these latter effects, no other noticeable change occurs in the studied spectral range upon cooling down to 7 K.

The modifications observed at 120 K in the spectra can be related to the NH_4 freezing, which occurs at about 120 K, and to the anomalous reduction of the lattice constant c around 120–150 K, observed by Ono *et al* (1991) in KADP-0.22.

4.2.2. Electric field polarized along the a axis. The infrared reflectivity spectra displayed in figure 2(*b*) correspond to the E modes active in KADP-0.3. The simulation of these spectra shows that the lattice mode frequencies are almost temperature-independent (figure 7(*b*)), confirming that the studied crystal preserves its tetragonal structure down to 7 K. The only noticeable features are the decrease of the TO oscillator strength of the lowest-frequency highly damped E mode, and the decrease of the internal mode frequencies upon cooling below 120 K (figure 7(*b*)).

The substitution of K^+ by NH_4^+ ions in the KDP crystal leads one to expect seven external lattice modes in KADP-x mixed crystals (Courtens and Vogt 1985). These external modes consist of K^+ and (NH_4^+)–$H_2PO_4^-$ translations, and $H_2PO_4^-$ and NH_4^+ librations. Our results displayed in figures 2(*b*) and 7(*b*) are in good agreement with this prediction: seven modes are observed below 300 cm^{-1}, in addition to the unexpected lowest-frequency E mode. The two expected ν_4 internal modes of the PO_4 groups are observed above 400 cm^{-1} (figure 7(*c*)). A supplementary mode is observed at 350 cm^{-1}, which could be assigned to the ν_2 internal mode of the PO_4 groups (figure 7(*c*)).

4.2.3. Dielectric behaviour in the low-frequency limit. Let us discuss now the effect of the onset of freezing on the dielectric constant of KADP-0.3 mixed crystal. As mentioned in sections 4.2.1 and 4.2.2, the low-frequency range, below 100 cm^{-1} for B_2 modes and 60 cm^{-1} for E modes, is dominated by a highly damped mode (figures 2 and 7) less polar than the corresponding modes in pure KDP and ADP. These low-frequency modes used in the fitting process of the experimental results (section 3) are not real lattice modes, symmetry-forbidden in pure compounds; rather, they correspond to a distribution of Debye-like relaxations (Simon and Gervais 1992).

The optical-modes contribution to the static dielectric constant ϵ_{lat} calculated through relation (3) allows one to estimate the dielectric constant at the limit of the infrared frequency range, i.e. 10 cm^{-1}. The results of the calculation respectively displayed in figures 5(c) and (d) for B$_2$ and E symmetry, evidence a clear decrease of both $(\epsilon_{lat})_c$ and $(\epsilon_{lat})_a$ upon cooling below 150 K. A similar behaviour was observed by Simon and Gervais (1992) for ϵ_c and ϵ_a in RADP-0.35. The decrease of ϵ_{lat} (figures 5(c) and (d)) is entirely due to the decrease of the TO oscillator strength of the lowest-frequency mode in both B$_2$ and E symmetries. These highly damped modes are due to collective proton hoppings, which obey the ice rule, i.e. preserves the configuration of two protons near each PO$_4$ group, coupled to other polar phonon modes (section 4.1.1). This decrease is due to the softening of some excitation below 10 cm^{-1}, which no longer contributes to the dielectric constant measured at this frequency.

It is to be noted that $(\epsilon_{lat})_c$ decreases below 150 K, while $(\epsilon_{lat})_a$ decreases below 125 K; these temperatures correspond respectively to the phase transition of pure ADP and pure KDP, but also to the temperature range in which Ono *et al* (1991) have observed the anomalous variation of the lattice constant c and the freezing of the NH$_4^+$ ions. These results allow us to define the temperature of the onset of freezing in KADP-0.3 mixed crystal between 120 and 150 K (figures 5(c) and (d)).

Let us now compare the obtained values $(\epsilon_{lat})_c$ with the temperature dependence of the dielectric constant ϵ_c of KADP-0.22, measured at 1 kHz by Ono *et al* (1991), which shows a broad rounded peak around 30 K, characteristic of the glassy state of the mixed crystals in the intermediate concentration range (Courtens 1982, 1987). Below 120 K, our results are much smaller than those of Ono *et al* (1991), while above 120 K, they are of the same order of magnitude. The same result is observed for $(\epsilon_{lat})_a$ when compared to the temperature dependence of ϵ_a measured at 100 kHz by Ono *et al* (1987). Thus a strong dispersion takes place between the infrared limit (10 cm^{-1}) and the very low-frequency range (Petzelt *et al* 1991, Simon and Gervais 1992). Dielectric measurements are now in progress in the low-frequency range in order to study the dielectric dispersion below the infrared frequency range.

4.3. Double-mode behaviour of the translational lattice mode polarized along the c axis

The activity of only one external B$_2$ symmetry lattice mode is expected from group theory, in the PE phase of both KDP and ADP (Bréhat and Wyncke 1985, Bréhat *et al* 1986). In fact, we have observed in the KADP-x mixed crystals studied, as in pure KDP and ADP, a symmetry-forbidden B$_2$ low-frequency strongly damped lattice mode, which was discussed in sections 4.1.1, 4.1.2 and 4.2. In addition to this mode, we did not observe one but two B$_2$ lattice modes, well separated in the case of KADP-0.3 (figures 1(a), 2(a) and 3(a)), which can be unambiguously assigned to separated K$^+$–H$_2$PO$_4^-$ and NH$_4^+$–H$_2$PO$_4^-$ external vibrations of translational character along the c axis. The lowest-frequency mode labelled Ω_1 is assigned to the external translational of KDP, while the highest-frequency mode labelled Ω_2 is assigned to that of ADP (table 1).

The assignment is supported by the results given in table 1, where we have reported the TO and LO mode frequencies together with the TO oscillator strength of the two B$_2$ lattice modes Ω_1 and Ω_2 at 250 K, obtained from the simulation of the experimental spectra of three KADP-x mixed crystals, and the B$_2$ lattice mode parameters of pure KDP and ADP. Table 1 shows that the TO oscillator strengths of mode Ω_1 decreases, while that of mode Ω_2 increases, with increasing ammonium

Table 1. Double-mode behaviour of the translational lattice mode polarized along the c axis in KADP-x mixed crystals at 250 K. Frequencies Ω_j (cm^{-1}) and TO oscillator strengths $\Delta\epsilon_j$ of the two modes Ω_1 and Ω_2.

	$K_{1-x}(NH_4)_x H_2PO_4$				
$E \parallel c$	KDP $x = 0$	$x = 0.01$	$x = 0.3$	$x = 0.97$	ADP $x = 1$
Ω_{1TO}	178	174	161	124	
Ω_{1LO}	280	234	176	129	
$\Delta\epsilon_1$	4.56	3.887	1.979	0.505	
Ω_{2TO}		239	223	200	192
Ω_{2LO}		278	282	286	297
$\Delta\epsilon_2$		0.12	2.612	3.455	4.10

concentration x, whereas these modes vanish in pure KDP and ADP. The double-mode behaviour of the translational lattice mode along the c axis is observed for all mixed crystals studied (sections 4.1 and 4.2).

In the case of KADP-0.97, the mode Ω_1 is not observed in the reflectivity spectra at 250 K (figure 3(a)), but is needed in the fitting process. Owing to its weak TO oscillator strength and to the value of its frequencies, this mode is merged in the low-frequency reflectivity band (figure 3(a)). In KADP-0.01, the Ω_2 mode appears as a shoulder in the high-frequency side of the reflection band corresponding to the translational lattice mode of KDP (figure 1(a)). It is only in the case of the mixed crystals of the intermediate concentration range that the two Ω_1 and Ω_2 modes are clearly observed in the experimental reflectivity spectra (figure 2(a)), as previously observed in RADP-x mixed crystals by infrared spectroscopy (Petzelt *et al* 1991, Simon and Gervais 1992) and Raman diffusion (Courtens and Vogt 1985, Lee and Kim 1988).

This translational mode is the only mode active in KADP-x mixed crystals to display a double-mode behaviour. Any mode polarized in a direction perpendicular to the c axis presents such a behaviour, because none of these modes is of pure translational character, these modes being rather of mixed translational and librational origin.

5. Conclusions

The present work constitutes the first infrared spectroscopic study of the KADP-x mixed crystal system, in the whole ammonium concentration range. In agreement with the previous dielectric measurements of Ono *et al* (1987), infrared spectroscopy shows that the mixed crystals can be classified into three groups according to the concentration x.

A PE–FE phase transition is observed from the temperature dependence of the infrared reflectivity spectra, in the ammonium-poor crystals, while a PE–AFE phase transition is evidenced in the ammonium-rich crystals (section 4.1). These phase transitions are quite similar to those observed in both pure compounds.

The crystals of the third group belong to the intermediate concentration range, $0.2 < x < 0.8$; they did not undergo any phase transition and maintain their PE tetragonal structure between 300 and 7 K (section 4.2). The crystals of this group form dipolar glasses below 120 K; the formation of the glassy state is manifested by a peculiar low-frequency dielectric behaviour observed from the analysis of the

infrared reflectivity spectra (section 4.2.3). Above 120 K, the infrared-active phonon modes behave like in both pure KDP or ADP, and show that no additional dielectric dispersion occurs in the low-frequency range below the overdamped B_2 and E modes. However, below 120 K, the lowest-frequency B_2 and E modes together with the optical modes, cannot explain the broad lower-frequency dielectric dispersion that appears upon cooling the mixed crystals down to 7 K. Thus the onset of freezing stands in the far-infrared spectral range, where the polarization fluctuations develop a broad distribution of Debye-like relaxations corresponding to the degrees of freedom which soften progressively upon cooling.

A second result evidenced by the present infrared spectroscopic study is the double-mode behaviour of the translational lattice mode polarized along the c axis, which is the only polar optical mode in the KADP-x mixed crystals to present such a behaviour owing to its pure translational character. This phenomenon, well known in mixed crystals of cubic symmetry, is characteristic of the KADP-x system, and it has been also observed in the RADP-x system.

Low-frequency dielectric measurements are in progress, together with infrared reflectivity spectroscopic and crystallographic studies of mixed KADP-x crystals of different ammonium concentrations.

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