Lattice vibrations in the mixed crystals (NH4I)0.3(KI)0.7, (ND4I)0.3(KI)0.7 and (NH4Br)0.3(KBr)0.7

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Abstract

Transverse optical phonons have been studied in $(NH_4I)_{0.3}(KI)_{0.7}$, $(ND_4I)_{0.3}(KI)_{0.7}$ and $(NH_4Br)_{0.3}(KBr)_{0.7}$ using Fourier-transform infrared techniques. In all materials three phonon modes have been observed in the far-infrared regime and were followed as a function of temperature in detail. While the first low-frequency mode characterizes a sublattice motion of the alkali ions against the halogenides $K^+ \leftrightarrow I^-$ and $K^+ \leftrightarrow Br^-$, the second mode involves vibrations of the ammonium molecules against the halogenide ions $NH_4^+ \leftrightarrow I^-$, $ND_4^+ \leftrightarrow I^-$ and $HH_4^+ \leftrightarrow Br^-$. Despite the fact that the average symmetry of these crystals is cubic, the transitional and orientational disorder locally breaks the cubic symmetry, the infra-red selection rules are relaxed and, hence, a third phonon contribution appears. Deviations of the temperature dependence of the eigenfrequencies, as expected for anharmonic modes, are interpreted in terms of a rotation–translation coupling where the phonon modes interact with the orientational degrees of freedom.

1. Introduction

The protonated and deuterated ammonium halides undergo a number of order–disorder phase transitions [1–3]. On cooling from room temperature, the α-phase ($Fm\bar{3}m$), in which the NH_4^+ ions reorient between eight symmetry-equivalent orientations, transforms into the β-phase ($Pm3m$), where only two energetically equivalent reorientations exist [3]. On further decreasing the temperature, octupolar order of the NH_4^+ molecules is established in the γ-phase within a tetragonal symmetry ($P4/nmm$). For the ammonium bromides an additional

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phase transition from the γ-phase, characterized by antiferrodistorsive ordering, into the δ-phase with ferro-ordering has been reported [2, 3].

KI and NH$_4$I are completely miscible [4]. The phase transitions of this mixed crystal system were studied in detail using different techniques [5, 6] and the phase diagram is well established [7, 8]. The mixed crystals reveal two additional phases, the ε-phase ($R\bar{3}m$) [9] and, at high potassium doping levels, an orientational glass (OG) phase [5, 10, 11], in which the reorienting moments freeze into random configurations. For many years orientational glasses served as conceptual links between phase- and glass-transtition phenomena and illuminated the physics of glassy freezing [5, 12]. The phase diagrams for the protonated and deuterated isomorphs are similar. Only the phase transition temperatures for the high-temperature plastic α-phase into the β- and ε-phases are significantly reduced in the deuterated isomorphs and in addition, the ε-phase appears in a much narrower concentration regime [13].

In this communication high quality single crystals of $(NH_4I)_x(KI)_{1-x}$, $(ND_4I)_x(KI)_{1-x}$ and $NH_4Br)_x(Br)_{1-x}$ with a nominal ammonium concentration of $x = 0.3$ were studied using Fourier-transform far-infrared spectroscopy (FIR), to investigate the temperature dependence of IR-active optical phonons. This concentration was chosen because no long-range structural phase transitions appear down to the lowest temperatures and an OG phase shows up in all crystals. Thus the temperature dependence of the phonons will only be due to anharmonic effects and due to the phase transition from the high temperature α-phase into the orientational glass phase at low temperatures. Similar experiments have been performed in the protonated and deuterated iodide systems [14, 15], but the optical excitation spectra in dipolar glasses at the freezing transition are far from being understood and have not been studied in detail.

We focused on the FIR regime, motivated to study the temperature dependence of the infrared-active optical phonons. A rotation-translation (RT) coupling between the TA phonon branch and the NH$_4^+$ orientations has been predicted theoretically [16] and has previously been studied by quasielastic and inelastic neutron scattering [17, 18] as well as by Brillouin-scattering techniques [19] for the protonated and deuterated ammonium iodide. It seems interesting to investigate whether the coupling to reorientational modes also affects the optical branches.

The protonated bromide system reveals a lattice parameter which is about 10% smaller than that of the iodide systems. For this system no phase diagram has been published so far. However elastic and quasielastic neutron scattering experiments revealed a quasielastic linewidth similar to that in the protonated iodide indicating the existence of an orientational glass state in these systems, too [20].

2. Experimental details

The single crystals have been grown from aqueous solutions and revealed a high optical quality without any polycrystalline inclusions. The single crystals investigated revealed lattice parameters of $a = 7.124$ Å for $(NH_4I)_{0.3}(KI)_{0.7}$, $a = 7.127$ Å for $(ND_4I)_{0.3}(KI)_{0.7}$, and $a = 6.647$ Å for $(NH_4Br)_{0.3}(KBr)_{0.7}$. The sample thickness for the transmission experiments was $d = 0.54$ mm for $(NH_4I)_{0.3}(KI)_{0.7}$, $d = 0.6$ mm for $(NH_4I)_{0.3}(KI)_{0.7}$ and $d = 0.72$ mm for $(NH_4Br)_{0.3}(KBr)_{0.7}$ and a thickness $d > 11$ mm has been chosen for all reflectivity measurements. For reflectivity and transmission measurements crystals with plane parallel faces with an area 8×7 mm^2 were used. The samples for both experimental set-ups were taken from the same batch.

The experiments were performed using the Brucker FT-IR spectrometer IFS 113v combined with an Oxford helium-flow cryostat with optical windows, allowing for reflectivity as well as for transmission measurements. Temperatures down to $T = 6$ K have been reached
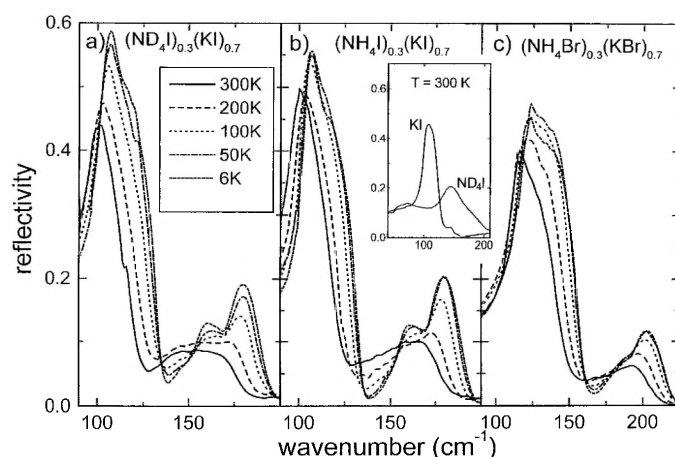
Figure 1. FIR reflectivity for several temperatures from $T = 6$ K to $T = 300$ K in the mixed crystals (a) $(ND_4I)_{0.3}(KI)_{0.7}$, (b) $(NH_4I)_{0.3}(KI)_{0.7}$ and (c) $(NH_4Br)_{0.3}(KBr)_{0.7}$. Note the different frequency scale in figure 1c. The inset presents the reflectivity spectra for the pure compounds KI and ND_4I.

with a temperature stability of $\Delta T = \pm 0.1$ K. All measurements were performed without polarizers because the crystals are optical isotropic (cubic symmetry) at all temperatures. The transmitted and reflected light was detected with a helium-cooled Si bolometer. Mylar beamsplitters of thickness 3.5 μm, 23 μm and 30 μm were used to record the spectra in the FIR regime. Subsequently the dielectric constant ε' and the dielectric loss ε'' were calculated from the reflectivity and transmission data using home-built software, which solves the non-linear equations for the reflectivity and the transmission [21]. From the resulting complex refractive index, the complex dielectric constant, $\varepsilon^* = \varepsilon' - i\varepsilon'' = n^2 - k^2 - 2ink$ was calculated taking the Kramers–Kronig relation into account.

3. Experimental results

The reflectivity and transmission spectra were measured for wavenumbers from 70 cm^{-1} to 700 cm^{-1} for $(NH_4I)_{0.3}(KI)_{0.7}$, $(ND_4I)_{0.3}(KI)_{0.7}$ and $(NH_4Br)_{0.3}(KBr)_{0.7}$ in the temperature range 6 K $\leqslant T \leqslant$ 300 K (see figure 1). In addition, the MIR and NIR regimes up to 8000 cm^{-1} were investigated for $(NH_4I)_{0.3}(KI)_{0.7}$ at room temperature.

At first we should like to focus on the reflectivity of the pure compounds KI and ND_4I, which have been measured at room temperature. The results are shown in the inset of figure 1. In the pure compounds reflectivity bands appear close to 100 cm^{-1} (KI) and 150 cm^{-1} (ND_4I), which approximately correspond to the frequencies of the optical phonons at the zone centre ($q = 0$) [22, 23]. The frequencies of the reflectivity bands are in good agreement with published IR results [2, 24, 25]. The small side band that appears close to 150 cm^{-1} in KI probably corresponds to a multiphonon contribution [24]. In the plastic phase of ND_4I the reorientational motion of the ND_4^+ tetrahedra introduces disorder and breaks the local symmetry. Consequently, phonon excitations of the whole Brillouin zone appear in the FIR spectra and, in addition to the zone-centre mode, a weighted density of states is observed. In the reflectivity spectra a peak appears for ND_4I at approximately 70 cm^{-1}, which probably can be attributed to the acoustic phonon excitations at the zone boundary. Between pure NH_4I and ND_4I no significant shift of the phonon excitation frequencies is expected.

The reflectivity of NH_4Br has already been studied [2] in the β-phase and the TO mode was located at about 160 cm^{-1}. In addition, the complete dispersion relations for KI [22], KBr [26] and ND_4I [23] were measured by inelastic neutron scattering. Optical absorption spectra at room temperature are summarized in [27]. Here minima have been observed approximately at 115 cm^{-1} for KI, at 150 cm^{-1} for ND_4I, at 120 cm^{-1} for KBr and at 160 cm^{-1} for NH_4Br, which coincide well with the phonon energies of the corresponding TO-phonon modes at the zone centre as detected in inelastic neutron-scattering spectroscopy [22, 23, 26]. These modes characterize a sublattice motion of the ions $K^+ \leftrightarrow I^-$, $NH_4^+ \leftrightarrow I^-$, $K^+ \leftrightarrow Br^-$ and $NH_4^+ \leftrightarrow Br^-$ corresponding to the displacement of the TO modes. A factor-group analysis yields the number of infrared-active modes. With respect to our experimental results the factor-group analysis in the harmonic approximation takes either $K^+ \leftrightarrow I^+$ or $NH_4^+ \leftrightarrow I^+$ vibrations into account. These irreducible representations are identical in the α-phase and the orientational glass phase with the same space group $Fm\bar{3}m$. The F_{1u} translational mode is expected only in the infrared spectra and the F_{1g} librational mode should be absent from both Raman and infrared spectra for the pure compounds. The Raman spectra of KI, KBr, NH_4I, ND_4I, and NH_4Br show no one-phonon scattering.

In the following we shall discuss the low-frequency reflectivities for the mixed crystals $(NH_4I)_{0.3}(KI)_{0.7}$ and $(ND_4I)_{0.3}(KI)_{0.7}$ for wavenumbers 90 cm^{-1} to 200 cm^{-1} and in the range from 90 cm^{-1} to 250 cm^{-1} for $(NH_4Br)_{0.3}(KBr)_{0.7}$ (see figure 1). Focusing on $(NH_4I)_{0.3}(KI)_{0.7}$ (figure 1(a)), at room temperature (solid line) the reflectivity increases from wavenumbers at 90 cm^{-1} and reaches a maximum at 100 cm^{-1} followed by a minimum and a second broad maximum at 160 cm^{-1}. With decreasing temperatures the peak maxima shift to higher wavenumbers and the maximum reflectivity at higher wavenumbers reveals a clear double-peak structure. The reflectivity spectra for the protonated iodide qualitatively behave very similarly. At room temperature in $(NH_4Br)_{0.3}(KBr)_{0.7}$ (figure 1(c)) both peaks appear at higher wavenumbers (115 cm^{-1} and 190 cm^{-1}) but a similar increase of the phonon frequencies appears on cooling. The reflectivity is small and nearly constant at higher frequencies up to 10 000 cm^{-1}; its value is determined by the optical permittivity ε_∞.

In addition, we investigated the temperature dependence of the transmission for all mixed compounds. The transmission of the iodides is plotted in the relevant region from 250 cm^{-1} to 450 cm^{-1} (figure 2(a) and 2(b)) and from 250 cm^{-1} to 550 cm^{-1} for the bromide sample (figure 2(c)). At low wavenumbers <250 cm^{-1} the transmission is almost zero and at wavenumbers <70 cm^{-1} absorption bands appear. At higher wavenumbers >500 cm^{-1} a strong increase towards the stretching excitations has been detected, which show up as broad absorption peaks at high wavenumbers similar to those found in CH_4 [27, 28]. Focusing on the spectra shown in figure 2, three minima were observed, which correspond to maxima in the absorption and result from multiphonon excitations in the crystals [14]. The strong increase influences the transmission spectra significantly, but at the relevant energies for the phonon excitations (see figure 1) no contributions from the transmission spectra can be detected.

From the reflectivity and transmission spectra we calculated the dielectric constant ε' and the dielectric loss ε'' as plotted in figures 3 and 4. At $T = 300$ K the dielectric constant ε' shows two extrema. On cooling two maxima develop from the peak at higher wave numbers in $(NH_4I)_{0.3}(KI)_{0.7}$ and $(ND_4I)_{0.3}(KI)_{0.7}$. In $(NH_4Br)_{0.3}(KBr)_{0.7}$ one peak remains down to the lowest temperature, $T = 20$ K. Accordingly, at low temperatures in the dielectric loss three maxima develop for iodides. For the bromide system a shoulder develops which hints toward a third contribution in this system, too. The maxima were attributed to transverse optical phonons at the Γ-point. On cooling the loss peaks shift to higher wavenumbers, increase in intensity and narrow in width. From the decreasing width we conclude that three modes contribute to the spectra already at room temperature.
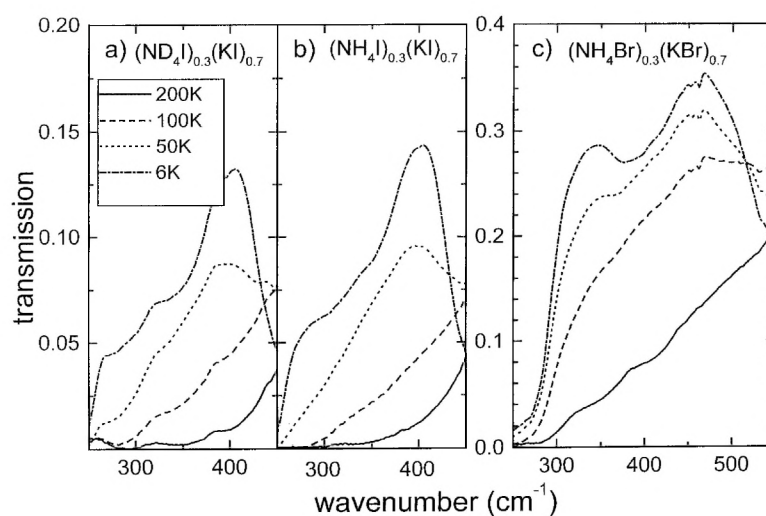
Figure 2. The FIR transmission spectra of (a) $(ND_4I)_{0.3}(KI)_{0.7}$, (b) $(NH_4I)_{0.3}(KI)_{0.7}$ and (c) $(NH_4Br)_{0.3}(KBr)_{0.7}$ for temperatures between $T = 6$ K and $T = 200$ K. Note the different frequency scale in (c).

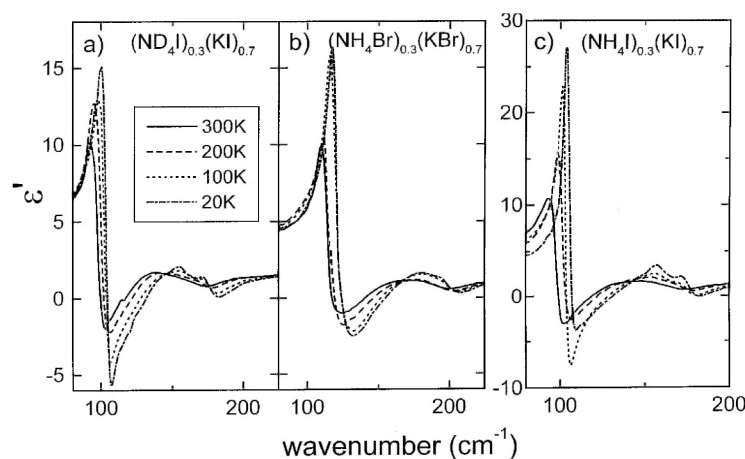**Figure 3.** Frequency dependence of the dielectric constant ε' for temperatures between 20 K and 300 K in (a) $(ND_4I)_{0.3}(KI)_{0.7}$, (b) $(NH_4Br)_{0.3}(KBr)_{0.7}$ and (c) $(NH_4I)_{0.3}(KI)_{0.7}$. For reasons of representation the bromide compound is shown in (b).

For the determination of the phonon frequencies a fit model was used which takes quasi-harmonic oscillators into account. Three oscillators have been fitted simultaneously, which described the observed spectra at each temperature satisfactorily. The temperature-dependent phonon frequencies are plotted in figure 5. Three temperature-dependent phonon modes appear in each of the three investigated systems. Comparing the reflectivity of the pure compounds KI and ND_4I (inset of figure 1) with the reflectivity in the mixed crystal system $(ND_4I)_{0.3}(KI)_{0.7}$ (figure 1(a)) we conclude that the first and second modes in the mixed compound $(ND_4I)_{0.3}(KI)_{0.7}$ have to be attributed to the sublattice motion of the ions $K^+ \leftrightarrow I^-$ and $NH_4^+ \leftrightarrow I^-$. The peak of the ND_4^+ versus I^- vibration is broader than expected already at room temperature. Thus we assume a third TO phonon branch at all temperatures. In a
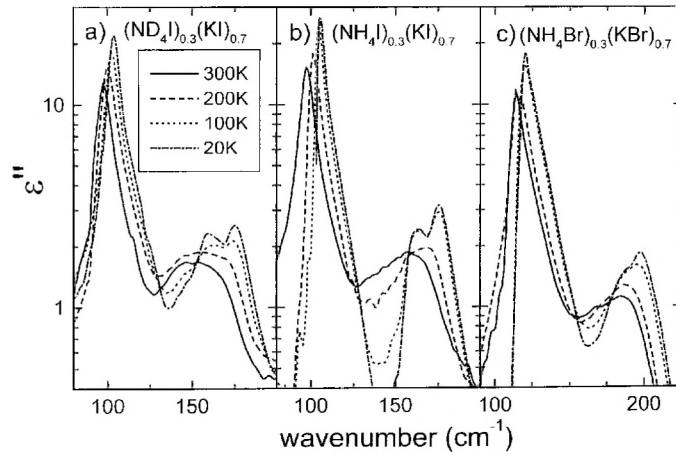
Figure 4. Frequency dependence of the dielectric loss ε^{μ} for temperatures between 20 K and 300 K in (*a*) $(ND_4I)_{0.3}(KI)_{0.7}$, (*b*) $(NH_4I)_{0.3}(KI)_{0.7}$ and (*c*) $(NH_4Br)_{0.3}(KBr)_{0.7}$.

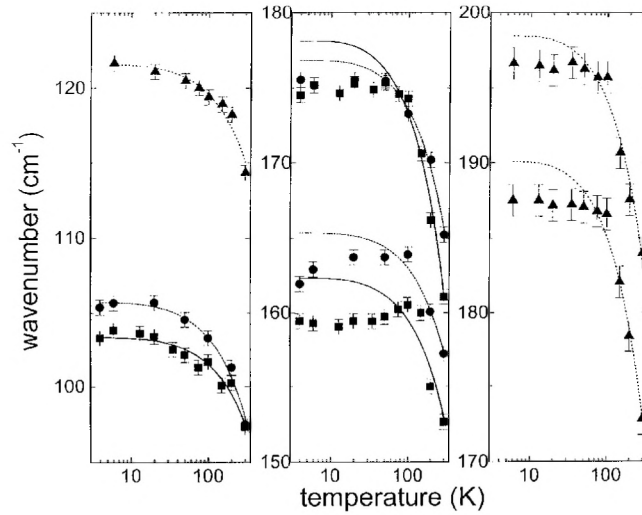**Figure 5.** Temperature dependence of the eigenfrequencies of the three dominant FIR modes in $(ND_4I)_{0.3}(KI)_{0.7}$ (■), $(NH_4I)_{0.3}(KI)_{0.7}$ (●) and $(NH_4Br)_{0.3}(KBr)_{0.7}$ (▲). The lines represent fits using an anharmonic model: $(ND_4I)_{0.3}(KI)_{0.7}$ (———), $(NH_4I)_{0.3}(KI)_{0.7}$ (- - - - -) and $(NH_4Br)_{0.3}(KBr)_{0.7}$ (· · · · · ·). The modes are shown in three different frequency regimes on a semi-logarithmic plot.

recent work by Kamba *et al* [14] a third phonon contribution was assumed to exist only for $T < 220$ K.

The phonon energies appear at the same positions as observed by neutron scattering [22, 23, 26]. We therefore conclude that the third peak results from a breakdown of the selection rules due to disorder, as usually is observed in orientational and dipolar glasses. The phonon energies of the TO modes remain nearly dispersionless in the pure compounds KI [23] and ND_4I [29] for the different wave vectors. We assume that the phonon excitations are only slightly broadened due to the fact that the full density of states contributes to the signal. The results of the other two materials are qualitatively similar.

With decreasing temperature all phonon eigenfrequencies shift to higher wavenumbers (figure 5) [29]. This increase results from anharmonic effects. The excitation energies of the transverse optical phonons of the bromides are higher than in the case of the iodides and it seems worth noting that the phonon modes of the protonated iodides are slightly enhanced compared to the eigenfrequencies in the deuterated iodides. The temperature dependence of the eigenfrequencies has been fitted using [30, 31]

$$\nu = \nu_0 - \Delta\nu / \left(e^{\frac{h\nu_0}{k_B T}} - 1 \right). \tag{1}$$

In figure 5 the calculated temperature dependences are plotted as solid lines for $(ND_4I)_{0.3}(KI)_{0.7}$, as dotted lines for $(NH_4I)_{0.3}(KI)_{0.7}$ and as dashed lines for $(NH_4Br)_{0.3}(KBr)_{0.7}$, respectively. ν_0 is the harmonic eigenfrequency at $T = 0$ K and $\Delta\nu$ is a frequency shift caused by anharmonic interactions.

The fits are in good agreement with the experimental results in the right-hand frame of figure 5, which describe the temperature dependence of the high-frequency modes for $(NH_4Br)_{0.3}(KBr)_{0.7}$. In contrast to this scenario the fits in the middle and left frames reveal significant deviations. In detail, the left frame of figure 5 shows the optical phonons, which can be attributed to the sublattice motion of the ions $K^+ \leftrightarrow I^-$ and $K^+ \leftrightarrow Br^-$, respectively. It can clearly be seen that the fits deviate for temperatures 30 K $< T < 100$ K.

The middle frame shows the temperature dependence of the frequencies of the sublattice motions $ND_4^+ \leftrightarrow I^-$, $NH_4^+ \leftrightarrow Br^-$ and of two phonons being IR active only via symmetry breaking. Clearly anharmonic effects alone are unable to describe the data sufficiently well and the temperature dependence of the phonons significantly deviates from the model predictions using equation (1).

The right frame of figure 5 shows the temperature dependence of the eigenfrequencies of the sublattice motion $NH_4^+ \leftrightarrow Br^-$ and of a disorder allowed mode. Surprisingly the fits are in good agreement with the experimental data, at least within the large error bars, which result from the uncertainty in determining the correct eigenfrequencies from the double-peak structures. The only simple explanation that could be given is that the coupling of the orientational degrees of freedom is frequency dependent and seems to be a maximum close to wavenumbers of 160 cm^{-1}.

The fit results are shown in table 1. From table 1 and figure 5 we conclude that the anharmonic shifts $\Delta\nu$ of the two modes at higher wavenumbers are significantly stronger than in the case of the $K^+ \leftrightarrow I^-$ vibration, in all investigated materials.

Table 1. Fit results of the temperature dependence of the transverse optical phonon modes in $(ND_4I)_{0.3}(KI)_{0.7}$, $(NH_4I)_{0.3}(KI)_{0.7}$, and $(NH_4Br)_{0.3}(KBr)_{0.7}$ using equation (1). ν_0 is the eigenfrequency for $T = 0$ K and $\Delta\nu$ indicates the strength of the anharmonic contribution.

	$(ND_4I)_{0.3}(KI)_{0.7}$		$(NH_4I)_{0.3}(KI)_{0.7}$		$(NH_4Br)_{0.3}(KBr)_{0.7}$	
	ν_0 [cm^{-1}]	$\Delta\nu$ [cm^{-1}]	ν_0 [cm^{-1}]	$\Delta\nu$ [cm^{-1}]	ν_0 [cm^{-1}]	$\Delta\nu$ [cm^{-1}]
mode 1	103.71 ± 0.30	4.38 ± 0.47	105.81 ± 0.24	5.03 ± 0.32	121.9 ± 0.28	6.06 ± 0.65
mode 2	161.5 ± 0.22	10.82 ± 1.75	164.4 ± 0.22	8.84 ± 1.32	187.3 ± 0.2	19.95 ± 0.28
mode 3	175.6 ± 0.22	20.01 ± 1.3	175.7 ± 0.2	14.1 ± 0.61	196.2 ± 0.3	21.01 ± 0.68

4. Discussion and conclusion

Three IR-active modes were detected for $(NH_4I)_{0.3}(KI)_{0.7}$, $(ND_4I)_{0.3}(KI)_{0.7}$ and $(NH_4Br)_{0.3}(KBr)_{0.7}$. The first mode is due to vibrations of the potassium sublattice against the hologenide ions, and the second mode corresponds to vibrations of the ammonium molecules

against the halogenide ions. The third mode obviously originates from symmetry breaking and hybridization effects in the mixed compounds. Here the temperature-dependent shift of the eigenfrequencies is rather strong. The temperature dependences of the phonon eigenfrequencies for both high-frequency modes reveal good agreement with fits using equation (1), taking only anharmonic effects into account. However, significant deviations of the temperature dependence as expected for anharmonic modes appear for the low-frequency modes.

Our crystal structure refinements showed that in $(NH_4I)_{0.3}(KI)_{0.7}$ no structural phase transition appears down to the lowest temperatures [8]. Hence, no phase transitions can influence the temperature dependence of the TO phonons and the anomalous behaviour can be ascribed to a coupling of the phonon modes to molecular reorientations.

In the present work we reported an unusual temperature dependence of TO-phonon modes. From Brillouin-scattering [19] and ultrasonic [17] measurements it has been concluded that the RT coupling should be largest at the X-point of the Brillouin zone. Due to rotational and translational disorder effects in these crystals phonons of the whole Brillouin zone have been observed in the FIR spectra, even above the OG transition. Based on neutron-scattering studies [18, 32] the RT coupling becomes dominant below $T = 80$ K, which is comparable to the temperature dependences of the TO phonons found in the present FIR data. We conclude that the RT coupling does not only influence the longitudinal [32] and transversal [18] acoustic phonons but also the transverse optical phonons. The strongest effects were detected in the TO modes, which originate from the $NX_4^+ \leftrightarrow I^-$ (X = H, D) vibrations. Smaller, but still significant effects were detected for the modes which involve motions of the alkali-metal ions against the halogenides. The temperature dependences of these low-frequency modes (left and middle frames of figure 5) do not follow the predictions for an anharmonic lattice and effects of the rotation-translation coupling are clearly observed. Only the high-frequency modes of the bromide system (right frame of figure 5) reveal no apparent effects due to RT coupling. As we do not expect a different behaviour of the bromide system as compared to the iodides, one explanation could be a frequency dependence of the rotation-translation coupling. Assuming that the rotational relaxation times are similar and that the different mixed crystals can be treated on the same footing, the strongest RT effects appear at 160 cm^{-1}. But much more theoretical work is needed to explain the coupling of optic phonon modes to molecular reorientations and to see whether the coupling also depends on frequency.

Acknowledgement

References

[1] Levy H A and Peterson S W 1953 *J. Am. Chem. Soc.* **75** 1536
[2] Perry C H and Lowndes R P 1969 *J. Chem. Phys.* **51** 3648
[3] Parsonage N G and Stavely L 1978 *Disorder in Crystals* (Oxford: Clarendon) pp 311 ff
[4] Havighurst R, Mack E and Blake F C Jr 1925 *J. Am. Chem. Soc.* **47** 29
[5] Fehst I, Böhmer R, Ott W, Loidl A, Haussühl S and Bostoen C 1990 *Rev. Phys. Lett.* **64** 3139
[6] Berret J F, Bostoen C and Hennion B 1992 *Phys. Rev.* B **64** 13 747
[7] Paasch M, Winterlich M, Böhmer R, Sonntag R, McIntyre G J and Loidl A 1996 *Z. Phys.* B **99** 339
[8] Güthoff F, Ohl M, Reehuis M and Loidl A 1999 *Physica* B **266** 310
[9] Paasch M, McIntyre G J, Reehuis M, Sonntag R and Loidl A 1996 *Z. Phys.* B **99** 333
[10] Winterlich M, Böhmer R and Loidl A 1995 *Rev. Phys. Lett.* **75** 1753
[11] Bostoen C, Coddens G and Wegener W 1989 *J. Chem. Phys.* **91** 6337

[12] Höchli U, Knorr K and Loidl A 1990 *Adv. Phys.* **39** 405
[13] Ohl M 2000 *PhD Thesis* University Augsburg
[14] Kamba S, Petzelt J, Pokorny J and Loidl A 1998 *Physica* B **244** 172
[15] Petzelt J, Kamba S and Gregora I 1997 *Phase Transitions* **63** 107
[16] Lynden-Bell J F and Michel K H 1994 *Rev. Mod. Phys.* **66** 721
[17] Berret J F, Sauvajol J-L and Hennion B 1992 *J. Phys.: Condens Matter* **4** 9235
[18] Berret J F, Bostoen C, Sauvajol J-L, Hennion B and Haussühl S 1991 *Europhys. Lett.* **16** 91
[19] Berret J F, Bruchhäuser F, Feile R, Bostoen C and Haussühl S 1990 *Solid State Commun.* **74** 1041
[20] Ohl M, Reehuis M, Schmidt W and Loidl A 2001 to be published
[21] Born M and Wolf E 1980 *Principles of Optics* (Oxford: Pergamon)
[22] Dolling G, Cowley R A, Schnitthelm C and Thorson I M 1966 *Phys. Rev.* **147** 577
[23] Vagelatos N, Rowe J M and Rush J J 1975 *Phys. Rev.* B **12** 4522
[24] Fertel J H and Perry C H 1969 *Phys. Rev.* **184** 874
[25] Durig J R and Antion D J 1969 *J. Chem. Phys.* **51** 3639
[26] Woods A D B, Brockhouse B N and Cowley R A 1963 *Phys. Rev.* **131** 1025
[27] Nyquist R A and Kagel R O 1997 *The Handbook of Infrared and Raman Spectra of Inorganic Compounds*
       No 4 (San Diego: Academic)
[28] Hollas J M 1996 *Modern Spectroscopy* (Chichester: Wiley)
[29] Buyers W J L and Crowley R A 1969 *Phys. Rev.* **180** 755
[30] Nelin G and Nilsson G 1974 *Phys. Rev.* B **10** 612
[31] Barron T H K 1965 Lattice Dynamics, Pegamon (New York) pp 247 ff
[32] Ohl M, Mayer F, Reehuis M, Schmidt W and Loidl A 2000 *Physica* B **274** 471