Lattice dynamics in perovskite-type layer structures. FIR studies of (CH₃NH₃)₂MnCl₄ and (CH₃NH₃)₂FeCl₄
Lattice dynamics in perovskite-type layer structures: FIR studies of \((\text{CH}_3\text{NH}_3)_2\text{MnCl}_4\) and \((\text{CH}_3\text{NH}_3)_2\text{FeCl}_4\)

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Abstract. The far-infrared reflectivity of \((\text{CH}_3\text{NH}_3)_2\text{MnCl}_4\) (= MAMC) and of \((\text{CH}_3\text{NH}_3)_2\text{FeCl}_4\) (= MAFC) single crystals was studied at several temperatures. By means of a Kramers-Kronig analysis, the frequencies of the long-wavelength infrared-active phonons were determined. Because of the considerable gap (300–900 cm\(^{-1}\)) between the external and the internal modes of the organic ions these can be treated as rigid bodies at far-infrared frequencies. In addition, we present the results of a structure analysis of MAMC above and below the continuous phase transition at 394 K which turns out to be of the order–disorder type. In the high-temperature tetragonal modification, three strong and two weak \(\text{IR}\)-active modes are observed for \(E\perp c\). From a comparison of the results with those obtained in materials with \(\text{K}_2\text{NiF}_4\) and perovskite structures, we conclude that the three strong modes and one of the two weak modes in MAMC and MAFC for \(E\perp c\) correspond to the three \(\text{IR}\)-active modes and the inactive mode in perovskite materials. While the second weak mode originates from a hindered rotation of the organic molecules.

1. Introduction

Bis-(alkylammonium)-metal-tetrachlorides \((\text{C}_n\text{H}_{2n+1}\text{NH}_3)_2\text{MeCl}_4\) crystallize in layer structures which are similar to the structure of \(\text{K}_2\text{NiF}_4\). If the divalent metal ion \((\text{Me}^{2+})\) is a paramagnetic one out of the iron group (e.g. \(\text{Mn}^{2+}, \text{Fe}^{2+}, \text{Cu}^{2+}\)), these compounds exhibit interesting magnetic properties. Due to the large geometrical separation of the \(\text{MeCl}_2\) planes, they are nearly ideal two-dimensional magnetic systems. For references see Mostafa and Willett 1971, Boesch et al 1971, de Jongh et al 1972, van Amstel and de Jongh 1972, Waldner and Boesch 1973, Heger et al 1973, Arend et al 1975. Among the methyl compounds (MA compounds), MACuCl\(_4\) (= MACC) orders ferromagnetically while the magnetic order in MAMnCl\(_4\) (= MAMC) and MAFeCl\(_4\) (= MAFC) is antiferromagnetic. In addition to the transition to a three-dimensional ordered antiferromagnetic state introduced by the weak interlayer interaction, there is a number of structural phase transitions in the latter two materials (Knorr et al 1974).

In a recent neutron diffraction study, the positions of the particles in the unit cell were determined, in addition to the crystal lattice parameters. From this study, some insight is obtained into the physical nature of the structural phase transitions. The transition at 394 K (\(\text{D}_{1h}^7\) to \(\text{D}_{2h}^5\), cf. table 1) is principally of the order–disorder type.
Above 394 K, MAMC has a disordered K$_2$NiF$_4$ structure where the MnCl$_6$ octahedra and the CH$_3$NH$_3$ molecules are distributed among four orientations with equal probability. Below 394 K, they are ordered in one of these orientations. In this context, measuring of lattice frequencies in the different phases will also provide some information about the phase transitions. Moreover, the intra- and interlayer interactions are of interest from the lattice dynamical point of view. As a consequence of the relatively large number of particles per primitive unit cell (one or two formula units for D$^{17}_{4h}$ or D$^{18}_{2h}$, respectively), the number of phonon branches is large and the phonon spectrum correspondingly complicated. However, it is possible to understand some of the lattice dynamical properties by means of a comparison to the properties of related and somewhat simpler structures.

The crystals of the general type, MAMEC, consist of perovskite-type layers, which are separated by the (CH$_3$NH$_3$)$^+$ ions. In the perovskite-type layers, the metal ions are surrounded by only slightly distorted Cl$_6$-octahedra. Therefore, the above mentioned comparison is performed with respect to the cubic perovskite structure and the structure of K$_2$NiF$_4$. These structures may be considered as consisting of the metal–halogen octahedra and the alkali or alkylammonium ions, respectively. From the lattice dynamical point of view, these two are the essential elements of the different crystals. It will be shown later, that the organic ions can be treated as rigid bodies in the analysis of the long-wavelength far-infrared (FIR) lattice frequencies.

The nearest-neighbour distance between Mn$^{2+}$ (or Fe$^{2+}$) ions and halogen ions within the octahedra is nearly the same for the different materials under comparison (e.g. Mn–F ~ 2.1 Å and Mn–Cl ~ 2.6 Å). Accordingly, the lattice parameters perpendicular to the c axis are almost unchanged in the series KMnF$_3$, K$_2$MnF$_4$ and MAMEC. On the other hand, the layer separation (lattice parameter c) changes drastically from KMnF$_3$ (c = 4.19 Å) to MAMEC (c = 19.48 Å). It is expected therefore that the intralayer interactions—both, magnetic and lattice dynamical—do not change appreciably in such a series of materials, while we cannot expect this behaviour for the interlayer interactions.

As a first step to obtain information about the lattice dynamics of the MAMEC compounds (Me = Mn, Fe), we have determined the frequencies of the infrared active phonons at $q = 0$ by means of FIR reflection measurements.

| Table 1. Structural and magnetic phase transitions of MAMEC. |
|---|---|---|
| Transition | Temperatures | Type |
| 394 K | continuous | tetragonal D$^{17}_{4h}$ |
| 257 K | discontinuous | orthorhombic D$^{18}_{2h}$ |
| 94 K | discontinuous | tetragonal D$^{18}_{4h}$ |
| 45 K | continuous | monoclinic |
| | | monoclinic antiferromagnetic |

† For the structural phase transitions of the Fe compound the corresponding temperatures are 328 K and 231 K, respectively. A low-temperature monoclinic phase could not be observed.
2. Experimental

Single crystals of MAMC and MAFC have been grown from aqueous solution as described earlier (Heger et al 1973, Knorr et al 1974). The faint pink platelets of MAMC are easily cleaved parallel to the above mentioned layers; the thickness of the platelets is about 3 mm and the area is several cm². The faint ochre MAFC samples are smaller platelets with a thickness of about 1 mm and an area of about 5 mm². At room temperature, the samples show considerable twinning not only when cooled down from the high-temperature tetragonal modification but also when grown at 300 K. It can be assumed that the two possible domains occur with equal statistical weight.

As MAMC and MAFC are weakly and strongly hygroscopic, respectively, precautions have to be taken in order to prevent excessive exposure of the samples to the water vapour of the air. When considering measurements on the high-temperature modifications of these materials, it should be noted that MAMC is destroyed at temperatures above 420 K-450 K and MAFC above 350 K.

The reflection measurements in the FIR spectral range from 15 cm⁻¹ to 800 cm⁻¹ have been performed with a commercial Fourier-transform spectrometer POLYTEC FIR-30 (Droste and Geick 1974, Geick 1974). An Oxford Instruments CF-100 continuous-flow cryostat was used to keep the samples at various temperatures between 10 and 410 K. The FIR radiation has been linearly polarized by means of polarizers (IGP 225 on KRS 5 substrate and IGP 223 on polyethylene substrate, purchased from Cambridge Physical Sciences). These polarizers have an efficiency of more than 90%.

Since crystals of the layer structures under consideration easily cleave parallel to these layers (i.e. perpendicular to the \( c \) axis), it is not difficult to prepare samples with sufficiently large areas (e.g. 25 × 10 mm) perpendicular to the \( c \) axis. With these samples there was no problem obtaining results for \( E \perp c \). However, it is extremely difficult to prepare large plane faces parallel to the \( c \) axis. Therefore, we tried at first to deduce the dielectric constant \( \varepsilon \) for \( E \parallel c \) from reflection measurements at an oblique angle of incidence on the large faces parallel to the layers. However, the experimental errors were so large, that only a crude estimate of \( \varepsilon \) for \( E \parallel c \) could be evaluated from the results. Consequently, reflection measurements on the small faces with \( E \parallel c \) turned out to yield more accurate results.

3. Results

3.1. Infrared spectra

The results of the reflection measurements at various temperatures are compiled in figure 1. The sample temperatures have been chosen in such a way that a reflection spectrum is obtained in each of the structural phases. Data are presented for both polarizations, \( E \perp c \) and \( E \parallel c \), in MAMC. Because of the rather thin MAFC samples no data could be obtained for \( E \parallel c \) for this material. On the whole, the measured spectra for MAMC and MAFC are very similar. Therefore, let us first consider the experimental results on MAMC.

Evidently, there are no restrahlenbands between 300 cm⁻¹ and 800 cm⁻¹ for all chosen temperatures. This is the case also for 20 K and 70 K where the data for 400–800 cm⁻¹ are not given in figure 1(a) and in figure 2(a) in order to be able to show the finer details of the spectra at these temperatures with an expanded frequency scale. The crude structure of the restrahlenbands as exhibited in the reflection spectra show
Figure 1. Reflection spectra of MAMC and MAFC at various temperatures. (a) MAMC for $E \perp c$, (b) MAFC for $E \perp c$, (c) MAMC for $E \parallel c$. 

FIR studies of lattice dynamics
Figure 2. Imaginary part $\varepsilon''$ of the dielectric constant of MAMC and MAFC at various temperatures. (a) MAMC for $E \perp c$, (b) MAFC for $E \perp c$, (c) MAMC for $E \parallel c$. 
three main peaks. But these are not clearly separated and there is considerable overlap, especially at high temperatures. This is due to the increase of damping with increasing temperatures. While there are very sharp peaks at low temperatures, the structure is smeared out already at 180 K, and at 410 K it is difficult to see the single peaks. As a consequence, there is an increase in experimental error with temperature. The eigenfrequencies can be determined at 20 K and 70 K with an error of 1 cm\(^{-1}\), while those at higher temperatures have an uncertainty of 2–3 cm\(^{-1}\).

For further discussions and in order to determine the eigenfrequencies, the damping and the oscillator strength of the various IR-active modes, it is necessary to deduce the imaginary part \(\epsilon''\) of the dielectric constant from the measured reflectivity \(R\). Therefore, a Kramers–Kronig analysis (KKA) of the reflectance was performed which led to the phase angle \(\theta\). From \(R\) and \(\theta\) the real and imaginary part of the dielectric constant \((\epsilon'\) and \(\epsilon''\)) have been evaluated (see figure 2). The fact that the exact value of the reflection could not be measured very well at very low and very high frequencies was a problem. Often the results of the KKA contained a negative phase angle at some frequencies. Then we performed a trial-and-error procedure within the limits of experimental error, the initial \(R\) spectra were varied and the KKA repeated. The most probable spectra are compiled in figure 1. From the more prominent maxima and shoulders of the \(\epsilon''\) spectra, the eigenfrequencies of the infrared-active modes have been deduced (see table 2). Tacitly, it has been assumed here that all these structures in the \(\epsilon''\) spectra are due to first-order and not to higher-order processes such as multiphonon or, below 45 K, two-magnon absorption. The oscillator strength of the modes and the halfwidth of the contributions to \(\epsilon''\) could only be estimated because of the overlap of the modes. The estimates are not given in the table. The attempt to fit the experimental data with a classical oscillator model did not yield much more reliable results due to the resulting ambiguities.

A comparison between the manganese and the iron compounds can be made only for \(E \perp c\), since no data are available for MAFC with \(E \parallel c\). There are no great differences between the \(\epsilon''\) spectra. Most of the eigenfrequencies are the same within a range of

| Table 2. Eigenfrequencies of the IR-active lattice modes at various temperatures. |
|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
|                  | MAMC \(E \perp c\) |                  |                  |                  |                  |                  |                  |                  |
| 20 K             | 72  80  84  91    | 91  110  118  127| 132  148  160  180| 226  234          |                  |                  |                  |                  |
| 70 K             | 72  79  85  97    | 97  116  125  130| 147  160  180  226| 233              |                  |                  |                  |                  |
| 180 K            | 95              | 120  160  180   | 230              |                  |                  |                  |                  |                  |
| 300 K            | 115             |                  | 145  150  185   | 230              |                  |                  |                  |                  |
| 410 K            | 111             | 120  145  165   | 220              |                  |                  |                  |                  |                  |
| (b) M AFC \(E \perp c\) | 72  79 102 111 | 112 125 165 175 | 222 230          |                  |                  |                  |                  |                  |
| 20 K             | 72  79 102 111  | 112 125 165 175 | 222 229          |                  |                  |                  |                  |                  |
| 70 K             | 74              | 102  126  165  | 227              |                  |                  |                  |                  |                  |
| 180 K            | 78              | 102  126  161  | 222              |                  |                  |                  |                  |                  |
| 300 K            | 78              | 102  126  158  | 220              |                  |                  |                  |                  |                  |
| 340 K            | 78              | 102  126  158  | 220              |                  |                  |                  |                  |                  |
| (c) M AFC \(E \parallel c\) | 72  82 100 109 | 112 122 145 152 | 168 180 224 236  |                  |                  |                  |                  |                  |
| 20 K             | 71              | 100  107  122  | 145  151  165  180| 225 236          |                  |                  |                  |                  |
| 70 K             | 93              | 112  145  164  | 198  232          |                  |                  |                  |                  |                  |
| 180 K            | 104             | 164  232          |                  |                  |                  |                  |                  |                  |
| 300 K            | 102             | 157  230          |                  |                  |                  |                  |                  |                  |
| 410 K            | 102             | 157  230          |                  |                  |                  |                  |                  |                  |
10 cm\(^{-1}\). A striking result is that in MAFC two eigenfrequencies are observed at about 75 cm\(^{-1}\) and 100 cm\(^{-1}\) for all temperatures, while in MAMC eigenfrequencies are found in this range only for low temperatures.

3.2. Structural data

For reasons of the close relation between the interpretation of lattice frequencies and phase transitions and the structure of our samples, we include the results of a structure analysis on MAMC at 404 and 293 K in this paper (cf. table 3). This analysis was performed by means of a neutron diffraction study on a single crystal of MAMC (= (CH\(_3\)

\[
\begin{array}{|c|c|c|c|c|c|}
\hline
\text{Atom} & \text{Occupation} & \text{Positional parameters} \\
& \text{I4/mmm} & \text{F4/mmm} & \text{probability} & x & y & z \\
\hline
\text{Mn} & 2a & 4a & 1 & 0 & 0 & 0 \\
& 4a & 1 & 0 & 0 & 0 \\
\text{Cl(1)} & 32o & 64o & 14 & 0.265(2) & 0.236(2) & -0.0118(3) \\
& 8e & 8e & 1 & 0.25 & 0.25 & -0.0125(8) \\
\text{Cl(2)} & 16m & 32m & 14 & 0.04(3) & 0 & 0.1273(3) \\
& 8f & 8f & 1 & 0.038(3) & 0 & 0.1285(6) \\
\text{C} & 4e & 8e & 1 & 0 & 0 & 0.3123(5) \\
& 8f & 8f & 1 & 0.059(5) & 0 & 0.314(1) \\
\text{N} & 32o & 64o & 14 & -0.032(6) & 0.014(6) & 0.3849(4) \\
& 8f & 8f & 1 & -0.024(4) & 0 & 0.389(2) \\
\text{H(1)} & 16m & 32m & 14 & 0.144(6) & 0 & 0.296(2) \\
& 8f & 8f & 1 & 0.171(8) & 0 & 0.307(3) \\
\text{H(2)} & 32o & 64o & 14 & -0.061(7) & 0.117(7) & 0.293(2) \\
& 16g & 1 & -0.011(4) & 0.075(27) & 0.273(10) \\
\text{H(3)} & 32o & 64o & 14 & -0.160(5) & 0.033(5) & 0.391(2) \\
& 8f & 8f & 1 & -0.161(5) & 0 & 0.388(2) \\
\text{H(4)} & 32o & 64o & 14 & 0.042(5) & 0.087(5) & 0.411(1) \\
& 16g & 1 & 0.007(2) & 0.085(25) & 0.418(7) \\
\hline
\end{array}
\]

\(\text{D}_{4h}^{2}(F4/mmm): a = 7.26 \text{Å}, \quad c = 19.5 \text{Å}\)

\(\text{D}_{2h}^{2}(Abma): \quad a = 7.28 \text{Å}, \quad b = 7.21 \text{Å}, \quad c = 19.4 \text{Å}\)

† The notation of the equipoints is that used in *The International Tables for x-ray Crystallography* (1969).

‡ For each atom, the positional parameters for the high-temperature modification (F4/mmm, 404 K) are listed in the upper line and those for the room-temperature modification (Abma, 293 K) in the lower line.

NH\(_3\)\(_2\)MnCl\(_4\)). A more complete presentation of this investigation will be published separately (Heger et al. 1975 to be published) including the experimental and technical details, e.g. the neutron diffractometer. From the complete structural information including the NH\(_3\) groups, a more profound knowledge of the mechanisms of the structural phase transitions of MAMC is expected. In the following, the structures of MAMC above and below the transition temperature 394 K are explained in detail in order to clarify the physical nature of the phase transition.

The high-temperature modification of MAMC crystallizes in the tetragonal space group D\(_{4h}^{2}\) (I4/mmm) with two molecules per unit cell. This is basically the K\(_2\)NiF\(_4\)
lattice type (Balz 1953) with a rather wide separation of the layers (see figure 3). The final positional parameters and occupation probabilities resulting from a least-squares refinement are given in table 3. The large disorder of the \((\text{CH}_3\text{NH}_3)\) groups and of the \(\text{Cl}^-\) ions seems to be typical for this highly symmetric structure. It was not possible to obtain a reasonable fit from our neutron diffraction data using the alternative model of continuously smeared out atomic distributions due to thermal vibrations.

![Diagram](image-url)

**Figure 3.** The high-temperature tetragonal structure of MAMC. (a) Unit cell of the I4/mmm structure. The \(x\) and \(y\) axes are chosen according to F4/mmm in order to match with those of the room-temperature modification. (b) One enlarged MnCl\(_6\) octahedron showing the different possible orientations of the Cl(1) and Cl(2). (c) One enlarged CH\(_3\)NH\(_3\) molecule. Only one position of the N atom is shown. The four-fold symmetry and the mirror-planes in \(xy\) and \(yz\) directions produce the other seven N positions.

The MnCl\(_6\) octahedra in the (001) planes are tilted randomly around the two equivalent [110] directions. Thus, every MnCl\(_6\) can have four different orientations, which have a reduced occupation probability \((\frac{1}{4})\). The (CH\(_3\)NH\(_3\)) molecule groups are aligned almost parallel to the \(c\) axis. Within the CH\(_3\) groups, the C atoms are located on the fourfold axis. Their strongly anisotropic thermal ellipsoids, whose major axes are perpendicular to the axis of high symmetry, could not be replaced by a split model description. For the H-atoms of CH\(_3\) a statistical distribution over 12 positions around \(c\) was found. In this way the threefold symmetry of the CH\(_3\) groups can harmonize with the fourfold one of the axis. It is remarkable that the independently refined H(1) and H(2) positions led within the standard deviations to a regular dodecagonal arrangement perpendicular to \(c\) with \(z = 0.295(2)\).
For the NH$_3$ groups the situation is much more complicated to describe. To begin with, it was not possible to locate the N atoms on the four-fold axis. Their eight positions with reduced occupation probability ($\frac{1}{8}$) form an octagon centred about $c$. Thus, the C–N bonds are situated on a cone around the axis. The three H sites associated with one N position form an equilateral triangle in a plane perpendicular to the particular C–N bond direction. Altogether, there are 16 H sites for the NH$_3$ group with unequal occupancies ($\frac{1}{4}$ and $\frac{3}{4}$). Principally a diffraction study, i.e. elastic scattering only, leads to a time-averaged structure picture. Besides the static description of the high-temperature structure of MAMC, we have to take into account transitions between the statistically occupied fixed point positions due to the high thermal mobility.

The room-temperature phase of MAMC crystallizes in the orthorhombic space group $D_{2h}^8$ (Abma or Cmca in the International Tables for X-ray Crystallography 1969). Its structure may be fully described with a moment picture of the high-temperature modification (see table 3 and figure 3). In this ‘frozen’ structure no disorder remains. The MnCl$_6$ octahedra layers are puckered, and the positions of Mn, Cl, C and N zig-zag along the $c$ axis in the (010) mirror-plane. The three H atoms of the CH$_3$ or NH$_3$ groups are symmetrically arranged with respect to the (010) plane. The triangles corresponding to the CH$_3$ and NH$_3$ protons are twisted by 180° with respect to one another. A striking deviation from the pure ‘frozen in’ model lies in the displacement of the CH$_3$ groups off the $c$ axis (cf. table 3). This might be described in terms of a tilting of the C–N dumbbells against the $c$ direction around their centre of gravity.

The results of our study of the two high-temperature modifications of MAMC as discussed in detail in this section lead to the conclusion that the second-order phase transition at 394 K in MAMC is mainly of the order–disorder type. The high-temperature tetragonal structure can be considered as a disordered modification of the room-temperature orthorhombic structure. The internal order parameter is the resultant occupation probability of one tilted molecular configuration ($0.25$ above the transition and $1.0$ below, cf. table 3). The additional displacement of the CH$_3$ groups with the transition (cf. table 3) may give rise to a soft mode the possibility of which was discussed recently on more theoretical grounds (Petzelt 1975, Kind and Roos 1975). Experimentally, Kind and Roos studied MAMC by means of $^{35}$Cl nuclear quadrupole resonance. Their results are in good agreement with our structure analysis.

3.3. Discussion

The infrared reflection spectra have been determined down to liquid helium temperatures, as already mentioned. However, a detailed discussion of the results will be possible only for the high-temperature tetragonal and the room-temperature orthorhombic modifications where the complete structural data are available for MAMC (cf. table 3). Also a group theoretical analysis with respect to the infrared-active lattice phonons can be done only for these two modifications. For MAFC which has the same crystal symmetry as MAMC (tetragonal at 340 K and orthorhombic at 300 K), we assume in this discussion that the actual structure of MAFC is very similar to that of MAMC and especially that the number of IR-active modes is the same for both materials in the high-temperature tetragonal and the room-temperature orthorhomic modifications.

For the high-temperature modification, a group theoretical analysis predicts that there are five IR-active modes for $E \perp c$ and three for $E \parallel c$. In this analysis the total number of particles per unit cell was not taken into account, but the organic ions were taken to be rigid bodies, which is justified for the discussion of the FIR external vibrations and
librations, since there is a considerable frequency gap to the internal vibrations (above 900 cm$^{-1}$, Arend et al 1975). A comparison with the experimental data shows that all modes predicted by group theory for the FIR region have been found and their eigen-frequencies have been determined assuming again that all the frequencies listed in table 2 are due to first-order processes.

The similarity of the observed spectra to those of perovskite materials is mainly due to three major peaks in the $\varepsilon''$ spectra. In crystals with perovskite structure and for $E||c$ in materials with perovskite-type layer structures (MAMC, MAFC, $K_2MnF_4$, $Rb_2MnCl_4$ etc.), these three peaks simply originate from the fact that there are three IR-active modes in these cases. For $E\perp c$, however, five IR-active modes contribute to the $\varepsilon''$ spectra in MAMC and MAFC. The estimated values of the oscillator strength defined by

$$\Delta \varepsilon = \int \frac{\varepsilon''(\nu)}{\nu} \, d\nu$$

are relatively large for three modes (in MAMC: $\Delta \varepsilon \approx 0.5, 2.4, \text{and } 1.1$ for $\nu_0 = 110, 145, \text{and } 220 \text{ cm}^{-1}$, respectively. They are smaller for the remaining two modes (in MAMC: $\Delta \varepsilon \approx 0.2$ for $\nu_0 = 120 \text{ and } 165 \text{ cm}^{-1}$).

For further interpretation, we performed some model considerations in which we compared the dynamical properties at $q = 0$ of materials with perovskite and perovskite-type layer structures. These model calculations are based on the experimental results presented here and also on unpublished data for $K_2MnF_4$ and $Rb_2MnCl_4$. Thus, we summarize here only some general results. For the four IR-active modes for $E\perp c$ in layer structures with point ions (e.g. $K_2MnF_4$), the force constants are in principle the same as for the three IR-active and one inactive modes in the perovskite structure (e.g. $KMnF_3$). Moreover the phonon frequencies of $K_2MnF_4$ at $q = 0$ are indeed close to those of $KMnF_3$ for $E||c$. But the oscillator strength of the mode inactive in $KMnF_3$ which becomes IR-active in $K_2MnF_4$ is relatively small. This can be understood from the eigenvectors of the modes in question. On these grounds, we identify the three strong modes and one of the two weak modes in MAMC and MAFC as corresponding to the three IR-active and the inactive modes in the perovskite structure, respectively. Then, the second weak mode is introduced by the hindered rotation of the molecules about the $x$ or $y$ axis.

For $E\parallel c$, the inactive mode of the perovskite structure and the rotation of the organic molecules about the $z$ axis are not IR active in the layer structure. As mentioned above, we deal only with three IR-active modes as in the perovskite structure. But in the layer structures, interlayer force constants enter the dynamical matrix and cause a considerable frequency shift (e.g. between $K_2MnF_4$ and $KMnF_3$).

Now let us turn to the room-temperature modification with orthorhombic symmetry. When compared to the high-temperature tetragonal modification, this can be viewed as an ordered form. However, this order requires the unit cell to be doubled. The consequence is a strongly increased number of long-wavelength lattice modes. The group theoretical reduction predicts that there are seven IR-active modes for $E\parallel c$, eight for $E\parallel a$ and six for $E\parallel b$. However, because of the twinning, 14 IR-active modes will be found experimentally for any polarization with $E\perp c$. These modes are spread over the relatively narrow range of 100 to 250 cm$^{-1}$ and cannot be resolved as their reciprocal life time or damping is about 30 cm$^{-1}$ at this temperature (Perry and Young 1967, Bürger et al
1975). If there is no frequency shift with temperature, the eigenfrequencies of the total 21
infrared-active modes at $q = 0$ and also those of the 24 Raman-active modes are equal to the
21 optical mode frequencies at $\Gamma$ (infrared-active, Raman-active and inactive) and to the
frequencies of the 24 modes at $X$ in the high-temperature modification (Petzelt 1975)
as can be shown by comparing the Brillouin zones of the two modifications.

At 180 K and lower temperatures, the temperature broadening has decreased
considerably. Therefore, it is hoped that a complete analysis of FIR experimental data
will be possible for the low-temperature tetragonal modification at 180 K and also
for lower temperatures. This analysis can be started as soon as the necessary data about
the crystal structure are available for these modifications.

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