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Infrared Activity of $KAl(MoO_4)_2$ and $NaAl(MoO_4)_2$

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We have investigated the infrared activity of phonons in monoclinic, pseudo-trigonal $NaAl(MoO_4)_2$ performing polarized reflectivity in the range 1200–700 cm^{-1} and IR absorption measurements of polycrystalline samples in the 1200–30 cm^{-1} region. To identify all modes predicted by group theory arguments, we compare the recorded spectra with similar measurements performed on trigonal $KAl(MoO_4)_2$. The obtained results allow us to propose the assignment of all observed bands to the respective vibrational modes. Our results suggest that the ambient temperature structure of $NaAl(MoO_4)_2$ may be described by the space group *C*2/*c*. © 1999 Academic Press

Key Words: **double molybdates; infrared spectra; phase transitions.**

INTRODUCTION

$NaAl(MoO_4)_2$ and $KAl(MoO_4)_2$ belong to the large crystal family of layered double molybdates and tungstates with the general formula $M^IM^{III}(M^{VI}O_4)_2$, where $M^I = Na$, K, Rb, Cs, $M^{III} = Al$, In, Sc, Cr, and $M^{VI} = Mo$, W. These compounds have been extensively studied because they exhibit interesting sequences of ferroelastic phase transitions (1–3). Interest in this class of materials has recently increased since the existence of incommensurate phases was reported in a few crystals belonging to this family (4–6). Furthermore, these compounds are of technical interest as suitable host crystals for a variety of inorganic phosphors.

In the present paper we report infrared study of $KAl(MoO_4)_2$ and $NaAl(MoO_4)_2$. The potassium molybdate crystallizes in the paraelastic, $P\bar{3}m1$ structure, with one molecule in the unit cell (7). The sodium derivative is ferroelastic at ambient temperature (1). Its structure is closely related to that of $KAl(MoO_4)_2$, but the symmetry is lowered due to slight displacements of Na^+ ions and rotations of MoO_4^{2-} tetrahedra. These displacements and rotations may be regarded as a result of a continuous, high-temperature phase transformation from the $P\bar{3}m1$ phase. Otko *et al.* (1) showed that the possible low-temperature phases might be described by $C2/c$, $C2/m$, $P\bar{1}$ space groups. The X-ray studies show that at ambient temperature $NaAl(MoO_4)_2$ is isostructural to $NaFe(MoO_4)_2$, which crystallizes in the monoclinic system. However, the conclusions concerning the space group of $NaFe(MoO_4)_2$ are not consistent, showing either $C2/c$ (8, 9) or $C2/m$ (10) structure.

The purpose of this study is to determine the nature of IR active modes, to relate the observed differences in the vibrational properties of the title crystals to the differences in their crystal structure, and, finally, to resolve the problem of the ambient temperature structure of $NaAl(MoO_4)_2$. These studies are complementary to our previous Raman investigation (11). We have also performed the temperature-dependent study of $NaAl(MoO_4)_2$ in the 93–493 K range, although our Raman measurements showed that the monoclinic structure was stable up to the melting point temperature (11). The measurements at different temperatures give, however, important information about the temperature dependence of frequencies and help us to understand the origin of IR active modes.

EXPERIMENTAL

Single crystals were grown by the method described previously (11). IR spectra were recorded with a Perkin–Elmer 2000 FT-IR spectrometer. The polycrystalline spectra were measured in KBr suspension in the region 1100–450 cm^{-1}. The far-IR spectra in the region 600–30 cm^{-1} were measured in Nujol suspension and the temperature-dependent spectra were recorded as CsI pellets. The reflection spectra were obtained with a Perkin–Elmer microscope operating under Auto-IMAGE software. The $NaAl(MoO_4)_2$ crystal used in this study was in a polydomain state. Therefore, the orientation of monoclinic axes was unknown. We can only say that the *y* axis is located within the plane perpendicular to the *c* period, because this axis is parallel to the two fold axis in the trigonal phase. All spectra were recorded with a resolution of 2 cm^{-1}.

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RESULTS AND DISCUSSION

Selection Rules

There are 36 ($k = 0$) vibrational modes for the $KAl(MoO_4)_2$ crystal of $P\bar{3}m1$ structure with one molecule in the unit cell. These modes may be subdivided into $A_{2u} + E_u$ acoustic modes, $2A_{1g} + E_g + 2A_{2u} + E_u$ stretching modes, $A_{1g} + 2E_g + A_{2u} + 2E_u$ bending modes, $A_{1g} + E_g + 2A_{2u} + 2E_u$ translational modes, and $A_{2g} + E_g + A_{1u} + E_u$ librational modes. In IR spectroscopy only A_{2u} and E_u modes are active.

The primitive cell of $NaAl(MoO_4)_2$ contains two molecules. The detailed analysis of differences in structural arrangement between the $KAl(MoO_4)_2$-type phase and the possible distorted phases was presented in a number of papers (1–3). Therefore, in this section we present only the results of our Factor Group analysis performed for the $C2/c$ and $C2/m$ structures. For the $C2/c$ structure the 72 ($k = 0$) vibrational modes are distributed among $A_u + 2B_u$ acoustic, $4A_g + 4B_g + 4A_u + 4B_u$ stretching, $5A_g + 5B_g + 5A_u + 5B_u$ bending, $4A_g + 5B_g + 6A_u + 6B_u$ translational, and $3A_g + 3B_g + 3A_u + 3B_u$ librational modes. In the case of the $C2/m$ structure the number of expected modes is the same as that found for the $C2/c$ structure, but the distribution among the irreducible representations is different. There are $A_u + 2B_u$ acoustic, $6A_g + 2B_g + 2A_u + 6B_u$ stretching, $6A_g + 4B_g + 4A_u + 6B_u$ bending, $6A_g + 3B_g + 4A_u + 8B_u$ translational, and $2A_g + 4B_g + 4A_u + 2B_u$ librational modes. The main difference between the $C2/c$ and $C2/m$ structures, of interest from the spectroscopic point of view, is the fact that in the $C2/c$ structure all molybdate tetrahedra are crystallographically equivalent (site symmetry C_1) whereas in the $C2/m$ phase the tetrahedra occupy two nonequivalent sites of C_s symmetry. As a result the A_{2u} modes of the trigonal phase are expected to be split either into $A_u + B_u$ or $2B_u$ modes in the $C2/c$ and $C2/m$ phase, respectively. As one can notice the polarization behavior of IR bands is expected to differ considerably, depending on the crystal structure. This fact, as is shown in the next section of this paper, allows the determination of the ambient temperature structure of the $NaAl(MoO_4)_2$ crystal.

Stretching Modes

Polycrystalline spectrum of $KAl(MoO_4)_2$ shows two weak bands at 976 and 932 and one strong band at 880 cm^{-1} (Fig. 1, Table 1). Our results are roughly in agreement with the data reported by Fomichev *et al.* (12), where the IR bands were located at 978, 935, and 890 cm^{-1}. The reflection spectrum in polarization $E \parallel c$ shows a weak band at 977 cm^{-1} and a strong band at about 920 cm^{-1} (Fig. 2). The spectrum recorded with light polarized perpendicular to the c period shows only one, very broad band with the maximum at about 905 cm^{-1}. Having in mind that the observed absorption maximum is expected to be at about the inflection point of the low-frequency part of the reflection spectrum, we may assign the 977 cm^{-1} reflection band (with the inflection point around 973 cm^{-1}) to the A_{2u} symmetric stretching mode ν_s observed at 976 cm^{-1} in the polycrystalline spectrum. In a similar way, the strong 905 cm^{-1} band, with the inflection point around 870 cm^{-1}, corresponds to the 880 cm^{-1} E_u asymmetric stretching mode. The location of the third predicted by factor group analysis mode, asymmetric stretch of A_{2u} symmetry, is more difficult. However, since the observed broad reflection band around 920 cm^{-1} is characterized by an inflection point similar to that of the E_u band, i.e., around 880 cm^{-1}, we may suppose that this band is also due to the E_u mode, which becomes active in polarization $E \parallel c$ due to defects or a slight misalignment of the crystal. Therefore, we may most likely assign the weak band at 932 cm^{-1}, observed for the polycrystalline sample, to the A_{2u} asymmetric mode. The large width of the E_u reflection band indicates that it is characterized by a large LO–TO splitting. However, we could not

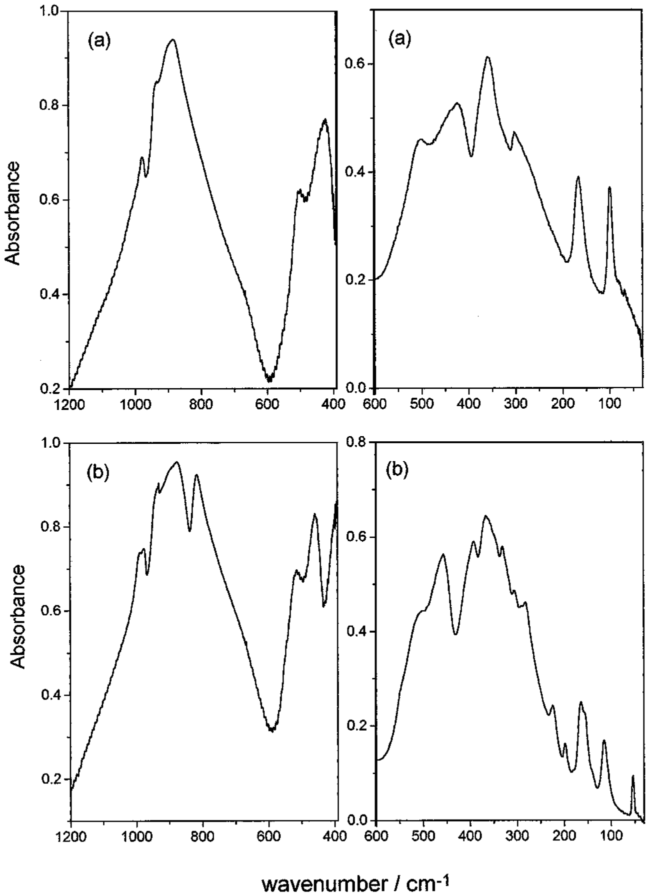

FIG. 1. Polycrystalline IR spectrum of $KAl(MoO_4)_2$ (a) and $NaAl(MoO_4)_2$ (b) at ambient temperature.

TABLE 1
Wavenumbers of IR Active Modes for Polycrystalline KAl(MoO$_4$)$_2$ and NaAl(MoO$_4$)$_2$

KAl(MoO$_4$)$_2$ (ν/c m^{-1})	NaAl(MoO$_4$)$_2$ (ν/c m^{-1})	Assignment
	988 w	ν_s(MoO$_4$)
976w	976 w	ν_s(MoO$_4$)
	934 w	ν_{as}(MoO$_4$)
932w	931 w	ν_{as}(MoO$_4$)
	889 sh	ν_{as}(MoO$_4$)
880s	876 s	ν_{as}(MoO$_4$)
	816 m	ν_{as}(MoO$_4$)
500m	503 m	T'(MoO$_4$) $*$ T'(Al^{3+})
423s	456 s	δ_s(MoO$_4$) and δ_{as}(MoO$_4$)
	392 m	
358s	366 s	
	331 w	
301m	306 w	T'(MoO$_4$) $*$ T'(Al^{3+})
	282 w	T'(MoO$_4$) $*$ T'(Al^{3+})
	224 w	T'(Na$^+$) and L(MoO$_4$)
	198 w	
165m	164 m	L(MoO$_4$) and T'(K$^+$)
	156 sh	
99m	115 m	T'(K$^+$) and T'(Na$^+$)
	53 w	Rigid layer mode

calculate the TO and LO frequencies since our attempt to perform the Kramers–Kronig analysis, using a commercially available software (Grams 386 Research), failed, possibly due to the appearance of the sharp *hole* band at 949 cm^{-1}. The origin of this effect is unknown. It resembles the structures observed in the stretching mode region of α-SiO$_2$ and α-AlPO$_4$ (13, 14). The observed dips were explained as a result of interaction between two oscillators of similar energy. However, in the case of KAl(MoO$_4$)$_2$, crystallizing in the $P\bar{3}m1$ structure, only one E_u stretching mode is predicted. The explanation, similar to that for quartz crystal, would require two E_u modes and would be possible if the crystal structure were described by the $P\bar{3}c1$ space group with two molecules in the unit cell. The $P\bar{3}c1$ structure differs from the $P\bar{3}m1$ one by only a slight distortion of the oxygen arrangement pattern and was unambiguously confirmed for KFe(MoO$_4$)$_2$ and KIn(WO$_4$)$_2$ crystals (7, 15). Recent studies of some other double molybdates, for example KSc(MoO$_4$)$_2$ (16), also showed that the structure might be refined with better discrepancy factor assuming the $P\bar{3}c1$ structure with two layers instead of the $P\bar{3}m1$ structure with one layer in the unit cell. However, this dip may also be explained as an extrinsic effect. Such sample-dependent effects were observed previously for α-SiO$_2$ and α-AlPO$_4$ in the 370–520 cm^{-1} region (13, 17).

The reflection spectrum of NaAl(MoO$_4$)$_2$, recorded in polarization $E \perp c$ (Fig. 3), shows three interesting features. First, the 949 cm^{-1} hole band is split into two components at 961 and 929 cm^{-1}. Second, a new band is observed at 816 cm^{-1}, which unambiguously originates from the E_u mode splitting. Finally, a weak band appears at 1000 cm^{-1}. The spectrum recorded in polarization $E \parallel c$ differs

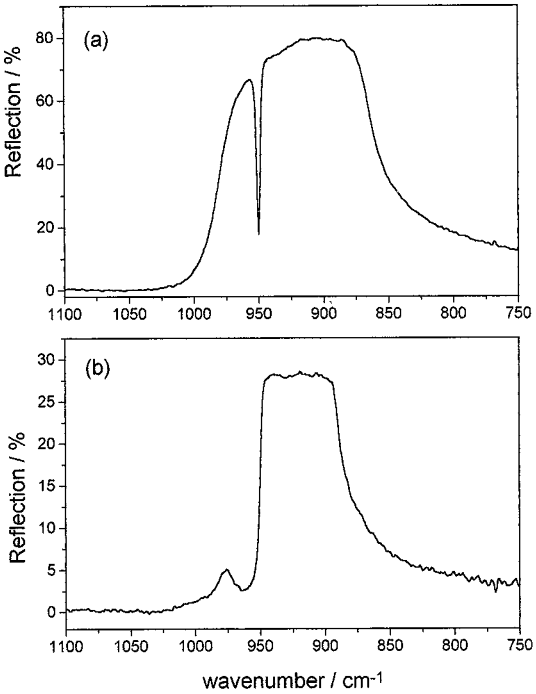

FIG. 2. IR spectrum of KAl(MoO$_4$)$_2$ recorded with light polarized perpendicular (a) and parallel (b) to the c period.

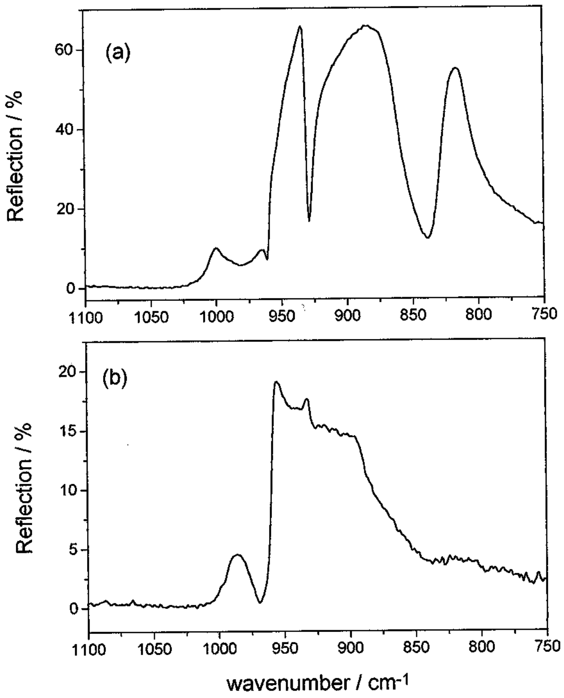

FIG. 3. IR spectrum of NaAl(MoO$_4$)$_2$ recorded with light polarized perpendicular (a) and parallel (b) to the c period.

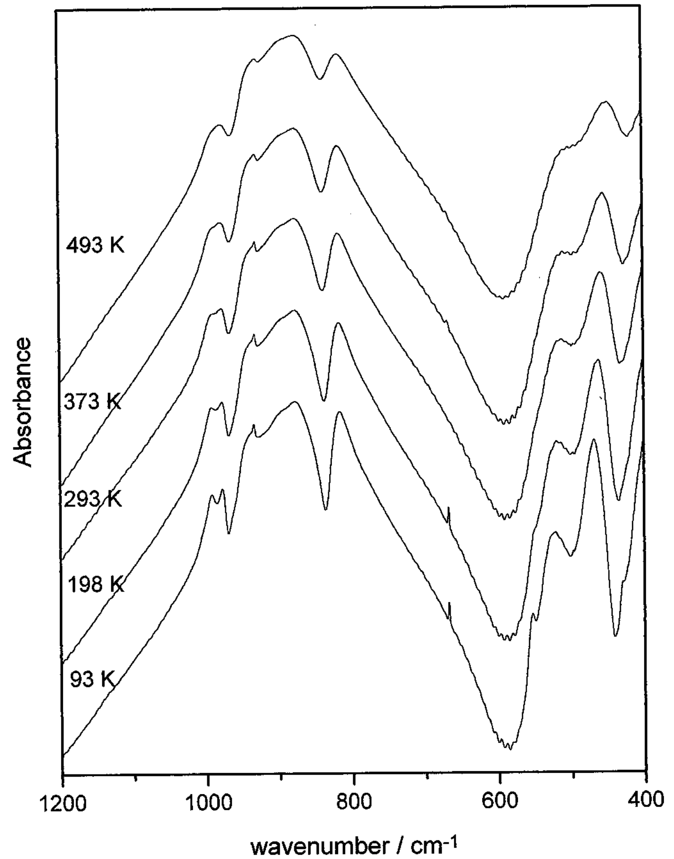

FIG. 4. Polycrystalline temperature-dependent spectra of NaAl$(MoO_4)_2$ in the stretching modes region.

significantly from that measured in polarization $E \perp c$. The ν_s mode is observed now at lower wavenumbers, i.e., 986 cm^{-1}, and the 816 cm^{-1} mode becomes very weak. Similar to $KAl(MoO_4)_2$, a relatively broad band appears also around 925 cm^{-1}. However, in the case of $NaAl(MoO_4)_2$ two additional narrow bands are observed on the top of this broad band at 955 and 932 cm^{-1}.

Let us now discuss the behavior of the stretching modes of $NaAl(MoO_4)_2$ in detail. The polycrystalline spectra, recorded in the 93–493 K range (Fig. 4), show that the intensity and frequency of the 976 cm^{-1} band remain unchanged up to 493 K, whereas the second 988 cm^{-1} band becomes very weak at 493 K and its intensity increases gradually with decreasing temperature. Such a behavior indicates that the 976 cm^{-1} band originates from the A_{2u} Brillouin Zone center mode of the trigonal phase, whereas the 988 cm^{-1} mode is the A-point *folded* mode. Since the monoclinic y axis is perpendicular to the c period and the A_u modes are active for $E \parallel y$ only, in polarization $E \parallel c$ only B_u modes may be observed. Our measurements show that in polarization $E \parallel c$ only one mode appears, at 986 cm^{-1}. Since its inflection point is around 977 cm^{-1}, this band may be related to the 976 cm^{-1} mode in the polycrystalline spectrum. Keeping in mind that for the $C2/c$ structure both ν_s components should exhibit different polarization behavior ($A_u + B_u$) and that for the $C2/m$ structure both components have the same symmetry B_u (see selection rules), the observation of only one B_u mode suggests that the crystal structure of sodium aluminium double molybdate at ambient temperature is described by the space group $C2/c$. The spectrum measured with $E \perp c$ gives additional arguments in favor of the $C2/c$ structure. For the polydomain crystal in this polarization both $A_u (E \parallel y)$ and $B_u (E \parallel x)$ modes are allowed by symmetry. These modes originate from the A_{2u} mode and in the trigonal phase the dipole change due to this vibration occurs along the c period. Since the $C2/c$ structure is derived from the $P\bar{3}m1$ structure by a slight rotation of molybdate tetrahedra around the x axis (3), where $y \parallel C_2$ and $x \perp C_2$, the resulting change of the dipole moment due to the ν_s vibration has for this phase a large component along the c period, a small component along the y axis, and zero component along the x axis. Therefore, we expect to observe only one mode in polarization $E \perp c$, of A_u symmetry. This is what we really observe (the 1000 cm^{-1} reflection band with the 991 cm^{-1} inflection point, which corresponds to the 988 cm^{-1} band in the polycrystalline spectrum). As observed for $KAl(MoO_4)_2$, the two bands originating from the A_{2u} asymmetric stretching mode in the trigonal phase, should be observed around 930 cm^{-1}. The 932 cm^{-1}, very narrow band superimposed on a much broader band around 925 cm^{-1} may be assigned to the folded A_u mode since it shows intensity increase with decreasing temperature. The second B_u band is observed easily in the polycrystalline spectra at 934 cm^{-1}. The appearance of the broad band in polarization $E \parallel c$ may have an explanation similar to that discussed for $KAl(MoO_4)_2$. The origin of the 955 cm^{-1} band, visible in the reflection spectrum only, is unknown. This mode might be the 959 cm^{-1} Raman active mode which becomes weakly IR active due to defects.

The doubly degenerate mode, of E_u symmetry in the trigonal phase, is split into two broad bands at 876 and 816 cm^{-1} in monoclinic $NaAl(MoO_4)_2$ due to the distortion of molybdate tetrahedra. The further splitting of these bands into Davydov doublets is observed for the 876 cm^{-1} mode only, which exhibits a shoulder around 889 cm^{-1}. The observed, very large splitting of the E_u mode (60 cm^{-1}) shows no change in the temperature range studied. The respective splitting of the Raman active E_g mode was 43 cm^{-1} and the clear decreasing of this splitting was observed with increasing temperature (11). Moreover, both IR absorption bands exhibit anomalous, strongly asymmetric shapes. The observed anomalous features may result from a resonant coupling between the discussed modes. It should be also emphasized that whereas the observed A_{2u}-type IR active modes differ from the A_{1g}-type Raman active modes by only a few reciprocal centimeters, the respective E_u-type modes are observed at much higher wavenumbers in comparison with the E_g-type ones. For $KAl(MoO_4)_2$ these modes are located at 880 (IR) and 800 cm^{-1} (RS), and for $NaAl(MoO_4)_2$ the respective pairs of modes are at 876 (IR) + 809 (RS) and 816 (IR) + 766 (RS) cm^{-1}. Such pronounced differences between the E_g and E_u-type modes indicate the large contribution of long-range coulomb forces to the E_u modes. Our previous IR and Raman studies of trigonal indium and scandium compounds (18) have shown that this contribution is also large for the indium compounds, although smaller than for the aluminum derivatives, and much weaker for the scandium compounds, where the observed respective IR and Raman wavenumbers differ not more than 22 cm^{-1}.

Bending and Lattice Modes

In the low-frequency region eight IR active modes are predicted by the factor group analysis for the $P\bar{3}m1$ structure. It is important to understand two significant differences in selection rules for Raman and IR active modes. First, the IR spectra give information about the translational modes of cations that cannot be obtained by the Raman technique. This is due to the fact that cations are situated at inversion centers in the $P\bar{3}m1$ phase and subsequently the respective modes are only IR active. Second, since the molybdate tetrahedra are strongly bonded to the aluminium ions in the layer and the potassium ions, situated between layers, are bonded very weakly, we may divide the four translational modes into two coupled modes $T'(MoO_4) * T'(Al^{3+})(A_{2u} + E_u)$ and two potassium translations $T'(K^+)$ $(A_{2u} + E_u)$. Since in Raman spectroscopy only pure translational modes $T'(MoO_4)$ are observed and in IR spectra the $T'(MoO_4)$ modes are coupled to the translational motions of light Al^{3+} ions, we may expect to observe the respective IR bands at frequencies much higher than we would expect to observe in the Raman modes. Having in mind that the pure $T'(MoO_4)$ modes are located at 175–164 cm^{-1} (11) for $KAl(MoO_4)_2$ and that frequencies of the coupled $T'(MoO_4) * T'(Al^{3+})$ IR bands should depend strongly on the atomic mass of the trivalent ion, we locate these modes at 500 and 301 cm^{-1} for $KAl(MoO_4)_2$, because in the isomorphous $KSc(MoO_4)_2$ crystal, where Al^{3+} ions are replaced by heavier Sc^{3+} ions, these bands are shifted to 405 and 266 cm^{-1}, respectively (18). The 500 cm^{-1} band has A_{2u} symmetry, since it does not split for the $NaAl(MoO_4)_2$ crystal (see Fig. 5). The 301 cm^{-1} band is of E_u symmetry and splits into 282 and 306 cm^{-1} components. The remaining two bands, located at 423 and 358 cm^{-1} for $KAl(MoO_4)_2$, are assigned to the bending vibrations. The comparison with $NaAl(MoO_4)_2$ shows that the former has A_{2u} symmetry, since it is observed as a singlet at 456 cm^{-1} for $NaAl(MoO_4)_2$, and the later is most likely the superposition of two E_u bands, since for $NaAl(MoO_4)_2$ two additional bands are observed on both sides of the 366 cm^{-1} band. These weak bands at 392 and 331 cm^{-1} originate from the E_u modes splitting.

The temperature-dependent spectra show a slight softening of bands originating from the E_u modes with increasing temperature (2–4 cm^{-1} in the 293–493 K range), whereas the 456 and 503 cm^{-1} modes, involving large motions of atoms along the c period, exhibit softening of 10 and 9 cm^{-1}, respectively. Similar strong temperature dependence was observed by us previously also for the A_{1g}-type Raman active bending and lattice modes (11).

In the region below 200 cm^{-1} only three modes are expected for the $KAl(MoO_4)_2$ crystal: $T'(K^+)$ of A_{2u} symmetry, $T'(K^+)$ of E_u symmetry, and librational mode $L(MoO_4)$ of E_u symmetry. In our measurements only two modes could be resolved at 165 and 99 cm^{-1}. The 99 cm^{-1} band is assigned by us to the $T'(K^+)$ since it shifts to 115 cm^{-1} for $NaAl(MoO_4)_2$. The 165 cm^{-1} band may be assigned to the second $T'(K^+)$ band, as has been shown in our studies of scandium compounds (18). However, it may be also assigned to the librational mode. Although librational modes were observed around 130–140 cm^{-1} for the scandium compounds, in the case of $KAl(MoO_4)_2$ we may expect to observe the librational mode at higher wavenumbers, by analogy with the behavior of E_u internal modes

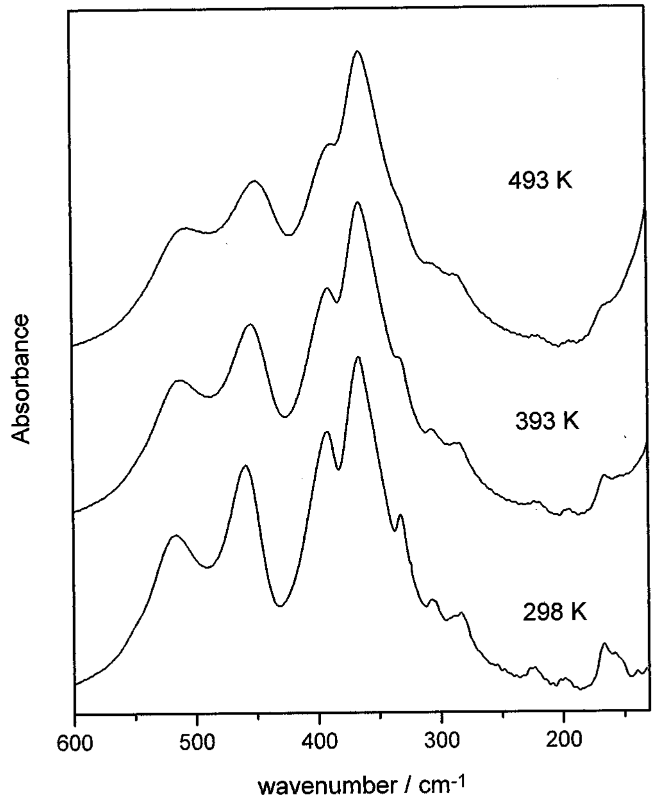

FIG. 5. Polycrystalline temperature-dependent spectra of $NaAl(MoO_4)_2$ in the bending and lattice modes region.

which are observed at significantly higher wavenumbers for $KAl(MoO_4)_2$ as compared to the scandium compounds. The assignment of the 165 cm^{-1} band to the E_u librational mode is also in agreement with the normal coordinate analysis performed by Fomichev *et al.* for the $KAl(MoO_4)_2$ crystal (12). Furthermore, the spectrum of $NaAl(MoO_4)_2$ seems also to support the proposed assignment since the 165 cm^{-1} band shows no shift toward higher wavenumbers when K^+ ions are replaced by Na^+ ions and it is split into two components at 156 and 164 cm^{-1}. The missing $T'(K^+)$ mode is most likely accidentally degenerate with the librational mode because the IR spectra of $NaAl(MoO_4)_2$ show two weak bands at 198 and 224 cm^{-1}, which may originate from the A_{1u} librational mode, which is inactive in the trigonal phase, and the $T'(Na^+)$ mode.

The remaining low-frequency mode at 53 cm^{-1} may be assigned only to the motions of layers as a whole, i.e., to the so-called rigid layer mode. Three such modes should be observed. One compressional-type originates from the A_{2u} acoustic mode and two shear-type from the splitting of E_u acoustic mode in the trigonal phase. The compressional mode is always observed at wavenumbers higher than those at which the shear-type is observed (19). Therefore, we can assign the 53 cm^{-1} mode to the motions of rigid layers along the *c* period. The shear-type modes could not be measured by us because these modes are probably located below the IR range that can be measured with the detector used in these studies.

CONCLUSIONS

The results obtained for monoclinic $NaAl(MoO_4)_2$ and trigonal $KAl(MoO_4)_2$ have proved to be very useful in determining the crystal structure of $NaAl(MoO_4)_2$ at ambient temperature. They allowed us also to propose the assignment of all vibrational modes to the respective motions of atoms in the unit cell and to establish the symmetries of all modes in the trigonal phase. These results are complementary to our Raman studies and show that the distortion of the $NaAl(MoO_4)_2$ unit cell is continuous. Another important observation obtained from these studies is the significant softening of the modes originating from the A_{2u} modes of the trigonal phase, especially bending and $T'(Al^{+3}) * T'(MoO_4)$ modes, confirming our previous conclusion drawn from the Raman studies that interlayer interactions play an important role in the stability of the crystal structure in this family of layered double molybdates.

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