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Raman scattering and lattice-dynamical calculations of crystalline KNO_3

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Abstract

The Raman spectrum of a KNO_3 single crystal was measured at both room and liquid-nitrogen temperatures. Lattice-dynamical calculations, based on the rigid-ion approximation and empirical potentials, were performed. The possibility of a phase transition at 217 K was investigated by measuring the temperature dependence of the Raman spectrum.

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The Raman spectrum of a KNO_3 single crystal was measured at both room and liquid-nitrogen temperatures. Lattice-dynamical calculations, based on the rigid-ion approximation and empirical potentials, were performed. The possibility of a phase transition at 217 K was investigated by measuring the temperature dependence of the Raman spectrum.

I. INTRODUCTION

The potassium nitrate crystal demonstrates strongly anharmonicity and dynamical disorder in its lattice-dynamical properties. Below 384 K, potassium nitrate is in so-called phase II, which has D_{2h}^{16} symmetry.[1] Above 403 K, it is designated in phase I, which is believed to have D_{3d}^{6} symmetry. It has a ferroelectric phase (phase III) between 384 and 398 K. Balkanski, Teng, and Nusimovici[1] reported Raman scattering at room and several higher temperatures. At room temperature, 12 of the 30 Raman active modes allowed by the symmetry-selection rules for phase II were observed. Two lines at 50 and 83 cm^{-1} had very strong intensities. Later Raman scattering work on KNO_3 was done by Brooker[2–4] and Akiyama, Morioka, and Nakagawa.[5] Brooker measured the Raman spectra of single-crystal KNO_3 at both room and liquid-nitrogen temperatures. He observed a broad asymmetry on the low-frequency side of the lattice mode at 52 cm^{-1} for the (ac) scattering configuration at room temperature. He associated this mode with the translational motion of K^+ ions against the NO_3 ions and interpreted the asymmetry as arising from the large amplitude of the motion and associated anharmonicity. Fermor and Kjekshus[6] performed electrical-resistivity and dielectric-constant measurements on KNO_3 at low temperature. They reported an anomaly at about 217 K and suggested that there is another phase transition at this low temperature. Lattice-dynamical calculations on KNO_3 were done by Rao *et al.*[7,8] and Akiyama, Morioka, and Nakagawa.[5] The former used a rigid-body approximation for the NO_3^- molecular ions. The values of their calculated frequencies were not reported. The latter was done by direct least-squares fitting of the force constants to the measured Raman frequencies.

There still remains much to be learned about the lattice-dynamical properties of KNO_3, such as the symmetry assignments of many lattice modes and further information about the anharmonicity and dynamical disorder. Also, a lattice-dynamical calculation based on analytical inter-ion potentials would be desirable, because it would provide a more physical description of the crystal, free of the kind of errors of numerical fitting of vibrational frequencies, which result from the uncertainty of the vibrational-mode assignments. In this paper we report experimental and theoretical studies of the lattice-dynamical properties of phase II of KNO_3. Raman spectra were measured at both room and liquid-nitrogen temperatures. Lattice-dynamical calculations were made, based on the rigid-ion approximation with empirical potentials. The force constants within the molecular group NO_3^- were obtained by numerical fitting of the internal vibrational frequencies. Since the internal modes of NO_3^- are well known, the numerical fits of these modes are free of the uncertainty of the mode assignments. Raman spectra in the lattice-mode region in the (ac) scattering configuration were measured at a series of temperatures to investigate the possibility of a phase transition at 217 K.

II. CRYSTAL STRUCTURE

Phase II of KNO_3 was determined by Nimmo and Lucas[9] to have an aragonite structure of D_{2h}^{16} orthorhombic symmetry. The lattice constants are $a=5.4142$, $b=9.1659$, and $c=6.4309$. As shown in Fig. 1, it has four molecules per unit cell and the negative nitrate ions stack directly above each other. The three oxygens in the nitrate ion are not exactly in a plane, and there is a slight bending of the ion. The coordinates of atoms in the unit cell[9] are listed in Table I. A complete symmetry analysis was given by Nusimovici.[10]

III. EXPERIMENTAL APPARATUS AND CALCULATION METHOD

Single crystals of KNO_3 were grown from an aqueous solution by slow cooling. The orientations of the crystal-

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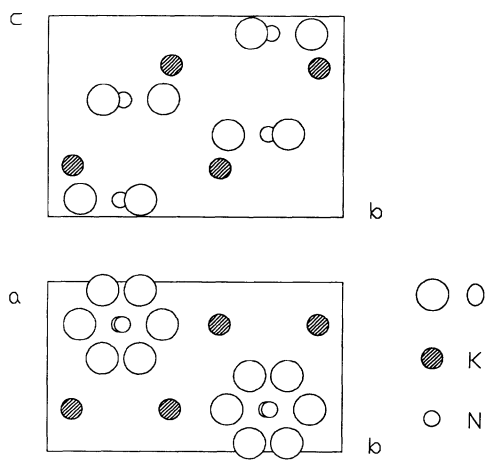

FIG. 1. Projection of the atoms onto the *ab* and *cb* planes for KNO_3 in the phase-II crystal structure.

lographic axes were identified by x-ray diffraction. The spectra were taken with the 514.5-nm line of a Spectra Physics 2016 Ar-ion laser and a Spex 1401 double monochromator. The laser power at the sample was about 80 mW. The monochromator slits were set to give a resolution of 2 cm^{-1}. The scattered light was detected with a photomultiplier and photon-counting electronics. The sample was placed inside a temperature-controlled cryostat, and the accuracy of the temperature control was within ± 0.1 K.

Lattice-dynamical calculations were made for KNO_3 phase II using a rigid-ion model with empirical potentials for the short-range forces. The empirical potentials used were of either one of the forms

$$V_{ij} = A_{ij} \exp(-r_{ij}/2) \tag{1}$$

or

$$V_{ij} = \frac{A_{ij}}{r_{ij}^5} , \tag{2}$$

where the A_{ij} are constants to be determined. For ions of the same sign, Eq. (1) was used, and for ions of opposite sign, Eq. (2) was used. Equation (1) is believed to give the better results of the two, but it cannot keep ions of different sign apart because it has a finite value at $r=0$. Also, potentials between ions of the same sign are expected to be different from those between ions of opposite sign. Different values of the coefficients A_{ij} were used for bonds of different lengths even when the ions in the pair were the same. This is because Eqs. (1) and (2) do not represent the real potentials. They can only be used to approximate the real potentials in the near neighborhood of the ion positions and cannot be used to describe the real potential for an extended range of inter-ion distances.

The calculation process was as follows. First, the five independent force constants of the nitrate ion, as deduced by symmetry, were found by fitting to the internal-mode frequencies of the NO_3^- ion. Then, with the NO_3^- ion and its calculated force constants, the forces on each ion of the unit cell, together with the stresses, were minimized by varying the constants A_{ij} of the empirical potentials between ions of the lattice. Only short-range potentials between nearest neighbors were considered. Experimentally measured ion positions were used; this is an advantage of this method, compared to a static relaxation approach, because some structure-related properties are conserved. The effective charges used to calculate the Coulomb forces were 1.0 for the potassium ion, 1.22 for the nitrogen ion, and -0.74 for the oxygen ion. It was found that about 17 parameters were needed to obtain a

TABLE I. Coordinates of atoms in the unit cell of *Pmcn* KNO_3.

No.	Atom	x/a	y/b	z/c
1	K	0.25	0.4166	0.7568
2	K	0.75	0.9166	0.7432
3	K	0.75	0.5834	0.2432
4	K	0.25	0.0834	0.2568
5	N	0.25	0.7548	0.9152
6	N	0.75	0.2548	0.5848
7	N	0.75	0.2452	0.0848
8	N	0.25	0.7452	0.4152
9	O	0.25	0.8902	0.9107
10	O	0.75	0.3902	0.5893
11	O	0.75	0.1098	0.0893
12	O	0.25	0.6098	0.4107
13	O	0.4492	0.6866	0.9151
14	O	0.5508	0.1866	0.5849
15	O	0.9492	0.3134	0.0849
16	O	0.0508	0.8134	0.0451
17	O	0.5508	0.3134	0.0849
18	O	0.4492	0.8134	0.4151
19	O	0.0508	0.6866	0.9151
20	O	0.9492	0.1866	0.5849

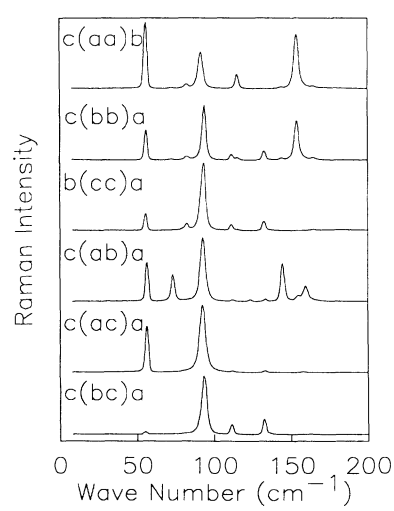

FIG. 2. Raman spectrum of KNO_3 at 78 K in the lattice-mode region.

TABLE II. Parameters in the lattice-dynamical calculation of KNO_3.

No.	A_{ij}	Bond
1	3.9605	K(1)—O(10)
2	6.1740	K(1)—O(12)
3	4.7385	K(1)—O(13)
4	4.4665	K(1)—O(14)
5	4.2864	K(1)—O(15)
6	−0.2880	K(1)—N(5)
7	−0.2682	K(1)—N(6)
8	−0.1393	K(1)—N(7)
9	−0.3723	K(1)—N(8)
10	0.0828	N(5)—N(8)
11	−0.0653	O(9)—O(16)
12	−0.1407	O(9)—O(16)(001)
13	0.1562	O(9)—N(8)
14	0.9001	O(9)—N(8)(001)
15	−0.0106	O(13)—O(18)
16	0.0744	O(13)—N(8)
17	0.1441	O(13)—N(8)(001)

sufficiently fast minimization of the forces. Finally, the vibrational frequencies of the crystal were calculated.

IV. EXPERIMENTAL AND CALCULATION RESULTS

The Raman spectra for KNO_3 were measured in the frequency ranges 6–250, 700–730, 810–840, 1000–1100, and 1300–1480 cm^{-1}. For certain scattering configurations, spectra in the range 850–1250 cm^{-1} were also measured. The spectra in the range 6–250 cm^{-1} at liquid-nitrogen temperature are plotted in Fig. 2. Note that the spectra for different scattering configurations are plotted on different scales. The spectra of the lattice mode region for (ac) scattering configuration at different temperatures are plotted in Fig. 3. The Raman frequencies at liquid-nitrogen temperature are listed in Table I.

The values of the 17 parameters obtained by minimizing both the forces on each atom and the stresses are listed in Table II. Angstrom was used as the unit of length, and the electron charge was used as the unit of charge. All of the calculated optical vibrational frequencies are positive. The values of the Raman frequencies are listed in Table III together with the measured ones.

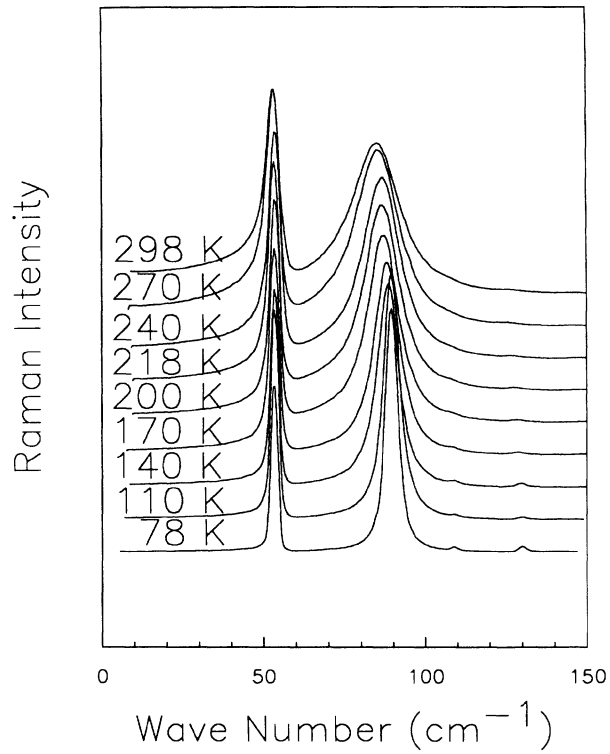

FIG. 3. (ac) Raman spectrum of KNO_3 taken at a series of temperatures.

V. DISCUSSION

A. Raman spectra

According to factor-group analysis,[1] there should be nine A_g (aa,bb,cc) modes, six B_{1g} (ab) modes, six B_{2g} (ac) modes, and nine B_{3g} (bc) modes. At liquid-nitrogen temperature, nine A_g modes, five B_{1g} modes, four B_{2g} modes, and six B_{3g} modes are identified. There are strong leakages in various scattering configurations. These leakages were also reported by earlier workers. Since phase II of KNO_3 has a quasihexagonal symmetry, it is very difficult to identify the refractive index axes in the a-b plane using two polarizers. This adds to the uncertainty in assigning the symmetry to various modes.

TABLE III. Experimental and calculated Raman frequencies of KNO_3 (in cm^{-1}).

	A_g			B_{1g}				B_{2g}			B_{3g}		
298 K	78 K	Calc.	298 K	78 K	Calc.		298 K	78 K	Calc.	298 K	78 K	Calc.	
53	56	44	67	73	72		53	56	45	83	94	84	
76	83	79		124	119		84	93	65	104	112	101	
108	116	107		145	122			138	143	124	133	134	
142	154	152	135	158	141				149		163	145	
159	165	169			196						165	148	
718	717	733			730	ν_4 of NO_3^-			726			730	ν_4 of NO_3^-
827	827	721				ν_2 of NO_3^-						820	ν_2 of NO_3^-
1054	1054	1045				ν_1 of NO_3^-							
1360	1361	1358	1348	1347	1354	ν_3 of NO_3^-		1393	1368		1456	1396	ν_3 of NO_3^-

At room temperature the lattice modes have large peak widths and many weaker peaks are not well defined, indicating the effects of the anharmonicity and dynamical disorder. Also, a very strong background is present in the low-frequency region of the Raman spectrum of KNO_3, especially in the (ac) configuration. The background in the (ac) configuration is many times higher than in other configurations and is about 100 times higher than from other crystals, such as K_2SO_4, studied on the same apparatus under similar conditions. The possible origin of this high background will be discussed later in conjunction with the discussion of the calculation results.

KNO_3 has several very strong external modes. This can be seen, for example, in the (ac) spectra. The intensities of these peaks are of the same order of magnitude as the totally symmetric A_g internal mode. This is in striking contrast to the Raman spectra of many other ionic molecular crystals, such as K_2SO_4, which have much lower intensities in the external-mode region than in the internal-mode region. KNO_3 and K_2SO_4 have about the same K—O bond lengths, and the electron density distributions on the potassium and oxygen ions are not expected to be much different. Thus the potassium and oxygen interaction cannot explain the extraordinarily strong Raman intensities in the external-mode region for KNO_3. On the other hand, as we mentioned earlier, in the KNO_3 crystal structure, the nitrate ions are stacked directly above each other. This stack forms a one-dimensional chain along the c direction in the crystal. Some interaction other than Coulomb interactions may be present between the stacked nitrate ions. This interaction could explain the very strong Raman intensities in the external-mode region of the crystal.

The three peaks at 56, 93, and 94 cm^{-1} are very strong and have large widths. The peak at 56 cm^{-1} is asymmetric and damps on the low-frequency side. Our calculation suggests that this mode is a combination of translational and rotational motion.

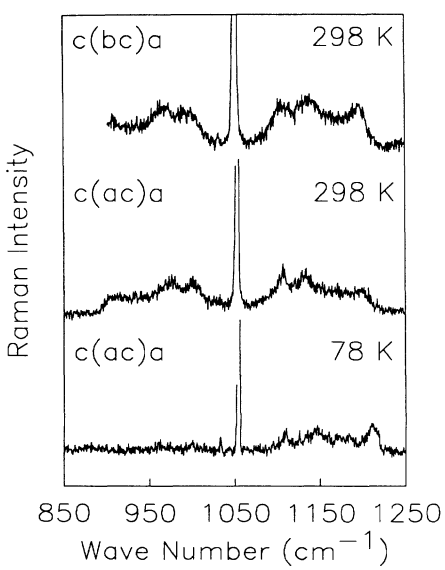

FIG. 4. Raman spectrum of KNO_3 showing higher-order scattering.

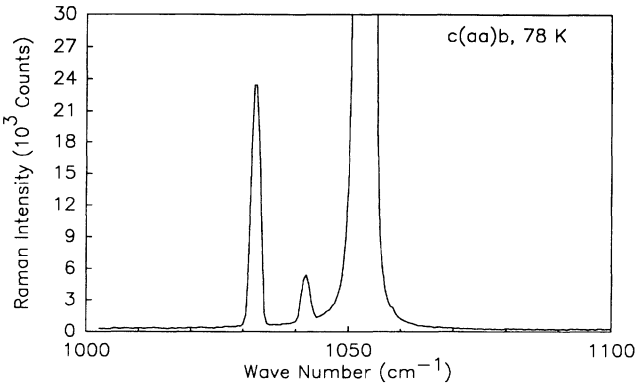

FIG. 5. Raman spectrum of KNO_3 showing isotope peaks of the totally symmetric internal mode.

As shown in Fig. 4, higher-order Raman spectra are found in the (ac) and (bc) configurations around the totally symmetric internal mode. At room temperature the left and right sides are symmetric about the totally symmetric internal mode. At liquid-nitrogen temperature, the left side disappears, indicating that these could be from higher-order Raman scattering. Three of these peaks can be observed, and their differences from the A_g internal-mode frequency are about 52, 83, and 148 cm^{-1}, indicating that there are strong interactions between the A_g internal mode and external modes of these frequencies.

As shown in Fig. 5, the two modes at 1032 and 1042 cm^{-1} can be identified as the isotope modes of the A_g internal mode. These are from the isotopes of oxygen ions, because for the totally symmetric A_g internal mode the nitrogen ion moves very little. The former is due to ^{18}O and the latter is due to ^{17}O.

B. Comparison between calculated and experimental results

From Table I it can be seen that the calculated Raman frequencies agree quite well with the experimental values. The calculation indicates there is an A_g mode at 43.6 cm^{-1} which is very close to the lowest B_{2g} mode at 45.4 cm^{-1}. This suggests that the peak measured in the Raman spectra of KNO_3 in the diagonal-polarization directions at about 55 cm^{-1} is not a leakage from the B_{2g} mode at 56 cm^{-1}, but a separate A_g mode itself.

The B_2 symmetry vibrational frequency of a free NO_3^- ion is infrared active but not Raman active. It has a frequency of about 820 cm^{-1}. In the KNO_3 II crystal, the coupling between the B_2 modes of the four nitrate ions in a unit cell produces two Raman-active modes, one of A_g symmetry and the other one of B_{3g} symmetry. However, the calculation gives a frequency of 721 cm^{-1} for the A_g mode, which is close to the frequencies of the E_2 modes of the free NO_3^- ion. Experimental results show that

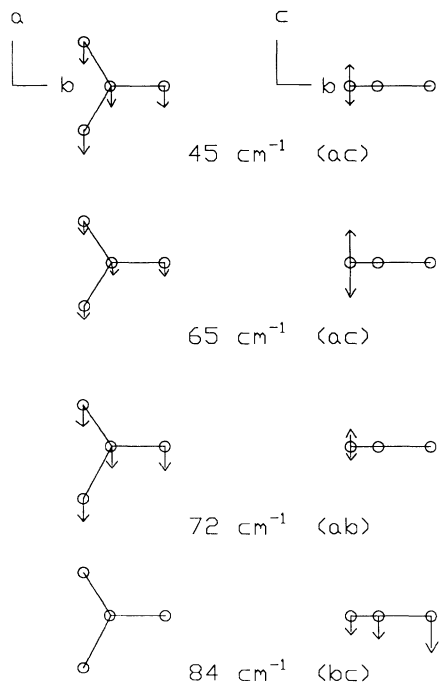

FIG. 6. Calculated eigenvectors of several Raman modes that have lowest frequencies.

there is a strong A_g peak at about 720 cm^{-1} and a weak A_g peak at about 820 cm^{-1}. One possibility is that the calculated frequency conversion is real and the weak peaks at about 820 cm^{-1} are due to the infrared modes with are activated by the anharmonicity and dynamical disorder. Thus it is inconclusive if the calculated frequency conversion is real or not, because the coupling between the four nitrate ions is weak compared to the interactions between ions inside the same nitrate molecule.

At room temperature there are several modes in the lattice-mode region which have strong intensities and large widths. It would be interesting to know with what kinds of ion motions these modes are associated. One can gain some information by examining the calculated eigenvectors associated with these modes. The eigenvectors of four of the lowest Raman frequencies are shown in Fig. 6.

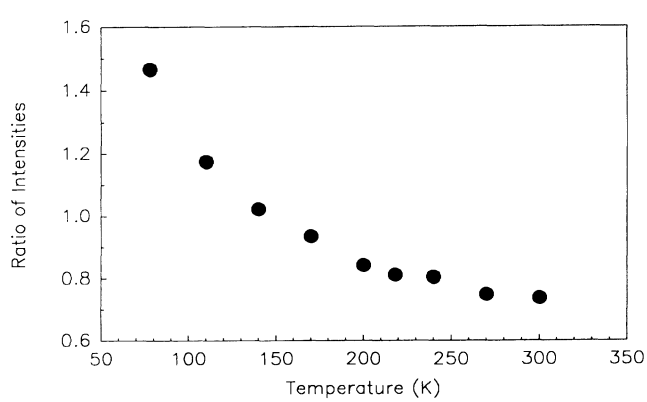

FIG. 7. Ratio of two Raman peak intensities in the (*ac*) configuration vs temperature.

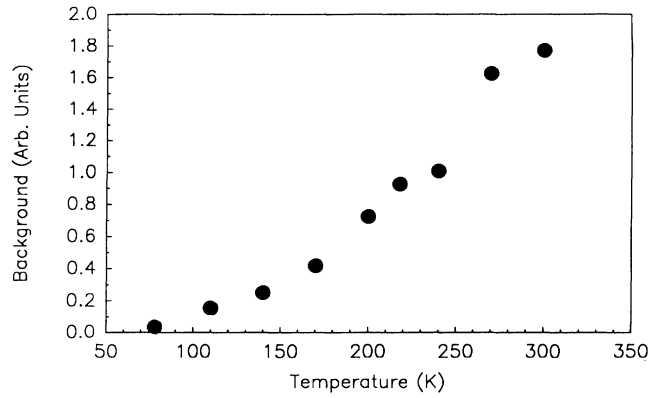

FIG. 8. Intensity of background in (*ac*) configuration vs temperature.

These modes are supposed to correspond to those strong and relatively broad peaks observed in the lattice-mode region in the measured Raman spectrum. It can be seen that most of them are a combination of translation and rotation. All the rotations are about *b* and *a* axes, and surprisingly, there is no rotation around the *c* axis. This is in contradiction to the previously held point of view that the dynamical disorder comes mainly from the rotation of the NO_3^- ions around the *c* axis. Instead, the strongest rotations are around the *b* axis. This seems consistent with the experimental observation that the strongest background is in the (*ac*) configuration, which is the rotation plane. Thus the high background observed in the Raman spectra of KNO_3 could be related to the disorder of these rotations of the nitrate ions around the *b* and *a* axes. These rotations generate light scattering because of the strong interactions between stacked nitrate ions. However, the theoretical study of phase transitions of KNO_3 (Ref. 11) suggested NO_3^- rotations around *c* axis at high temperatures.

C. Possible phase transition at 217 K

Fermor and Kjekshus[6] reported anomalous values for the electrical resistivity and dielectric constant and suggested a phase transition in the vicinity of 217 K. To investigate this, Raman spectra of the external modes in the (*ac*) configuration were measured at a series of temperatures ranging from liquid-nitrogen to room temperature. The results are plotted in Fig. 3. The values of the ratios of the two strongest peak are plotted versus temperature in Fig. 7, and the magnitude of the background is plotted against temperature in Fig. 8. There is no apparent evidence of a phase transition in the vicinity of 217 K from these data.

VI. SUMMARY

The Raman spectra of KNO_3 single crystals were measured at both room and liquid-nitrogen temperatures. The results agree well with those of other workers. Several external Raman modes have very large intensities that are attributed to interactions between stacked nitrate

ions. A high background was found in the low-frequency region, especially in (*ac*) spectra. This is attributed to the distortion of the rotational vibrations of the nitrate ions around the *b* axis. Higher-order Raman spectra were found in the (*ac*) and (*bc*) configurations, suggesting a strong interaction between the totally symmetric internal and external modes.

The results of lattice-dynamical calculations agree reasonably well with experiment. The eigenvectors of some very strong lattice modes were examined. They were found to be a combination of translation and rotation. All these modes have large rotations around the *b* axis, and there are no predominant rotations around the *c* axis.

(*ac*) Raman spectra for the external-mode region were measured at different temperatures to look for a phase transition in the vicinity of 217 K. No evidence of a phase transition was observed.

ACKNOWLEDGMENTS

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