

## LATTICE DYNAMICS AND PHASE TRANSITIONS

# The Cubic-to-Monoclinic Phase Transition in $(\text{NH}_4)_3\text{ScF}_6$ Cryolite: A Raman Scattering Study

A. N. Vtyurin\*, A. Bulou\*\*, A. S. Krylov\*, M. L. Afanas'ev\*, and A. P. Shebanin\*\*\*

\* Kirensky Institute of Physics, Siberian Division, Russian Academy of Sciences,  
Akademgorodok, Krasnoyarsk, 660036 Russia  
e-mail: vtyurin@iph.krasn.ru

\*\* Université du Maine, Le Mans, Cedex 9, 72085 France

\*\*\* Institute of Geology, Siberian Division, Russian Academy of Sciences,  
ul. Akad. Koptyug 3, Novosibirsk, 630090 Russia

Received May 8, 2001

**Abstract**—This paper reports on a Raman study of the cubic-to-monoclinic phase transition in  $(\text{NH}_4)_3\text{ScF}_6$  cryolite. We observed sharp anomalies in the frequencies and half-widths of the Raman lines corresponding to internal vibrations of the  $\text{ScF}_6^{3+}$  ions and to lattice vibrations; no soft lattice mode condensation was revealed. It is concluded that the phase transition studied is related primarily to the orientational ordering of these ions.  
© 2001 MAIK “Nauka/Interperiodica”.

## 1. INTRODUCTION

Cryolites are a family of perovskite-like crystals ( $Fm\bar{3}m$  space group of the undistorted structure,  $Z = 4$ ). They appear to be promising subjects for investigation both as having application potential and as model media for use in studying phase transition (PT) mechanisms [1]. Investigation of the phase transitions occurring in fluorine compounds of this family is usually complicated by their fairly high temperatures; the presence of ammonium ions in the structure reduces the phase transition temperatures [2], thus making them particularly attractive for investigation.

It is presently established that in most ammonium-containing cryolites, phase transitions are associated with orientational motion of the  $\text{MeF}_6^+$  and  $\text{NH}_4^+$  molecular ions and that the sequence of the phase transformations, their temperatures, and mechanisms vary substantially depending on the radius of the trivalent cation [2]. In the  $(\text{NH}_4)_3\text{ScF}_6$  cryolite, phase transitions were observed to occur in the order  $Fm\bar{3}m$  ( $Z = 4$ )  $\longleftrightarrow$   $P12_1/n1$  ( $Z = 2$ )  $\longleftrightarrow$   $I12/m1$  ( $Z = 16$ )  $\longleftrightarrow$   $I\bar{1}$  ( $Z = 16$ ), with the transition points  $T_1 = 330$ ,  $T_2 = 293$ , and  $T_3 = 243$  K, respectively [2, 3]. The cubic symmetry of the high-temperature phase (shown in Fig. 1) assumes that at least one of the ammonium ion sublattices [denoted by  $(\text{NH}_4)_I$  in Fig. 1] is orientationally disordered (the corresponding ion local symmetry is  $O_h$ ); it thus appears logical to assume that the observed sequence of the phase transitions (or, at any rate, the first of them) is associated with the ordering of these ions. At the same time, it was pointed out in [2, 3] that the entropy change

at the first PT is too large to be accounted for by the ordering of the  $\text{NH}_4^+$  ions alone and the possibility of simultaneous orientational ordering of the  $\text{ScF}_6^{3+}$  sublattice occurring in this transition was suggested. The present work is aimed at establishing the part played by the molecular ions in the mechanism of this transition.

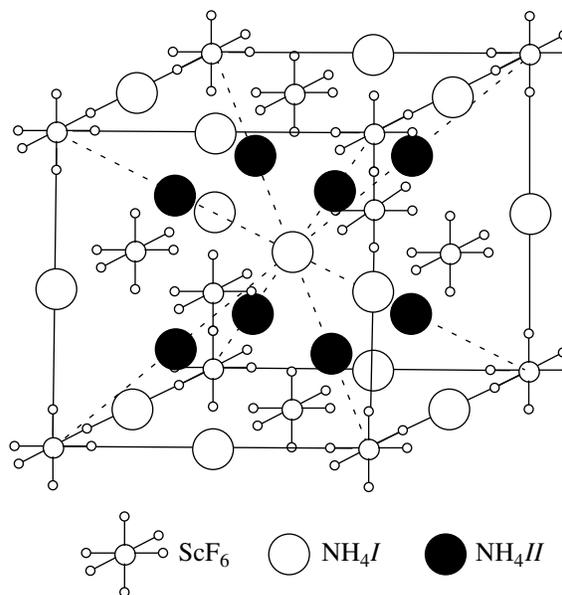


Fig. 1. Structure of the cubic phase of  $(\text{NH}_4)_3\text{ScF}_6$ .

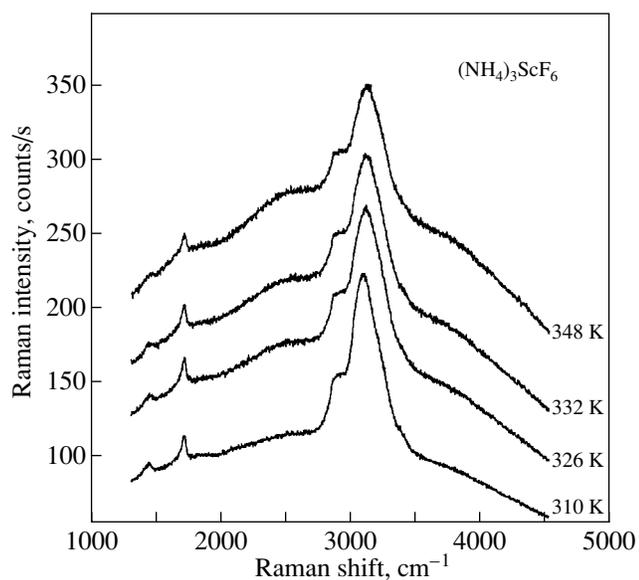
## 2. EXPERIMENT

The compound was prepared by reacting equivalent amounts of  $\text{NH}_4\text{F}$  with  $\text{Sc}_2\text{O}_3$  in HF (10%). Faceted single crystals were grown through slow controlled evaporation of a neutral saturated aqueous solution at 305 K over 8 months. The crystals were thin rectangular plates with well-developed faces (typically measuring  $5 \times 5 \times 0.5$  mm); they did not contain defects or inclusions visible under a microscope and were used in spectral measurements without any additional processing. The spectra were obtained on Jobin Ivon U-1000 and T-64000 Raman spectrometers with CCD detector arrays and a set of microattachments. In the latter spectrometer, the high-frequency spectra of the broad bands of internal ion vibrations were measured in a single-monochromator arrangement, while in the region below  $1000 \text{ cm}^{-1}$ , triple-monochromator arrangement with dispersion subtraction was employed to suppress the elastic-scattering wing as much as possible; the low-frequency cut-off was at  $8 \text{ cm}^{-1}$ . The spectral slit width was varied from  $5 \text{ cm}^{-1}$  (at high frequencies) to  $1 \text{ cm}^{-1}$ , the spectral range of the CCD array cell used in the triple monochromator arrangement was  $650/1024 \text{ cm}^{-1}$ , and the signal accumulation time was up to 600 s. The excitation was provided by polarized 514.5-nm radiation from a 200-mW  $\text{Ar}^+$  laser. The phase transition occurring at  $T_1 = 330 \text{ K}$  is essentially first-order, and it is accompanied by considerable spontaneous sample

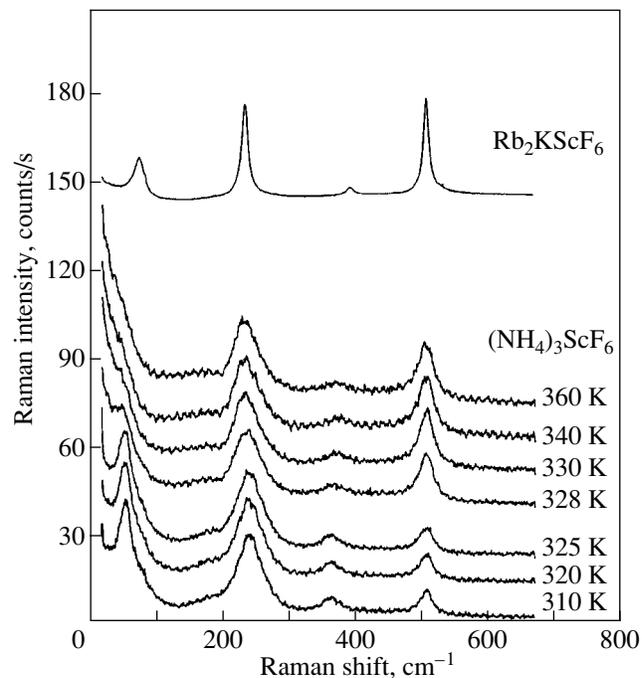
deformation; in this connection, special measures were taken to preclude local heating and defect formation at the laser focal point. The sample temperature determined during spectral measurements was stabilized to within 0.2 K.

## 3. RESULTS AND DISCUSSION

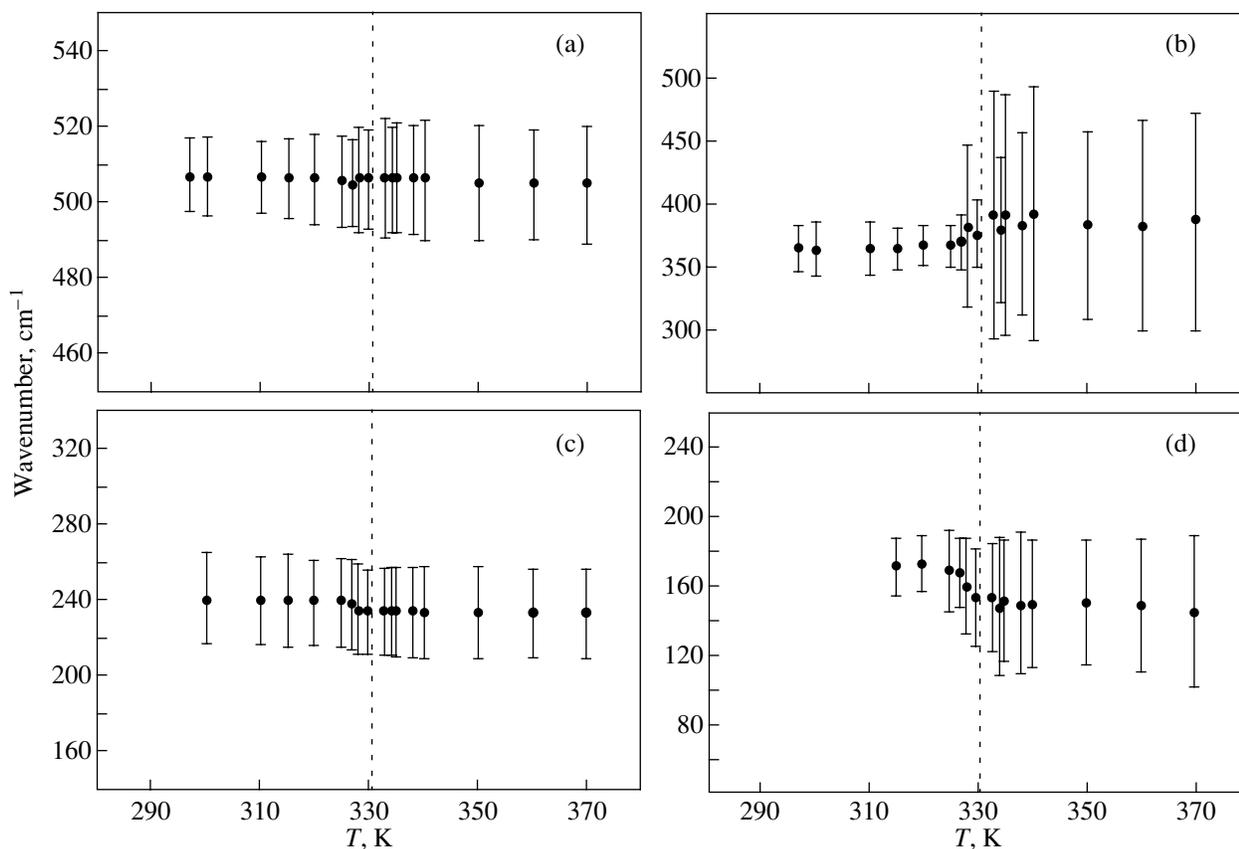
Because of the earlier conjecture of the ammonium sublattice being possibly involved in the mechanism of the phase transition under study, we first studied the high-frequency part of the Raman spectrum ( $1200\text{--}4500 \text{ cm}^{-1}$ ), which includes the internal vibrations of these ions. Figure 2 shows the evolution of these spectra with temperature. We readily see that the spectra vary very little in this region; there are no sharp changes in the region of the (first-order) phase transition, and the background, which is apparently associated with the increasing contribution of the well-known strong anharmonicity of the  $\text{NH}_4^+$  ion vibrations, grows steadily. The large linewidths, particularly in the  $2800\text{--}3500 \text{ cm}^{-1}$  interval (of the order of hundreds of wavenumbers), which corresponds to the internal valence vibrations of this ion [4], may originate both from strong anharmonicity and from orientational disorder on the ammonium sublattices. The considerable anharmonicity of these modes is also indicated by the intensities of the broad, double-phonon bands near  $2500$  and  $3700 \text{ cm}^{-1}$ , which grow with temperature.



**Fig. 2.** Spectra of internal ammonium ion vibrations of the  $(\text{NH}_4)_3\text{ScF}_6$  crystal.



**Fig. 3.** Transformation of the low-frequency part of the  $(\text{NH}_4)_3\text{ScF}_6$  spectra with temperature. For comparison, a spectrum of the isomorphous cubic phase of  $\text{Rb}_2\text{KScF}_6$  is shown.



**Fig. 4.** Temperature dependences of the frequencies and line half-widths (shown by vertical lines) of (a)–(c) the internal  $\text{ScF}_6$  ion vibrations and (d) the ammonium sublattice phonon vibration.

The second spectral region studied by us ( $8\text{--}650\text{ cm}^{-1}$  in Fig. 3) includes internal vibrational modes of the  $\text{ScF}_6$  molecular ions and lattice vibrations. The octahedral site symmetry in the cubic phase coincides with the free-ion symmetry; thus the selection rules also coincide: the Raman-active free-ion vibration frequencies are  $\nu_1(A_{1g}) = 498\text{ cm}^{-1}$ ,  $\nu_2(E_g) = 390\text{ cm}^{-1}$ , and  $\nu_5(F_{2g}) = 230\text{ cm}^{-1}$  (the frequencies and notation were taken from [4]). The frequencies obtained for the cubic phase are  $510$ ,  $385$ , and  $240\text{ cm}^{-1}$  (values contained for  $360\text{ K}$ ), which indicates weak distortion of the ions by the lattice. At the same time, the lines are strongly broadened. For comparison, Fig. 3 also shows an unpolarized room-temperature spectrum of the isomorphous cubic phase of  $\text{Rb}_2\text{KScF}_6$ ; one readily sees that the half-widths of the corresponding spectral lines in the crystal under study are a few times larger.

According to the selection rules for the cubic phase (see [5] for a comprehensive analysis), its Raman spectrum should contain one lattice-phonon line corresponding to the translational vibration of one of the ammonium sublattices (with  $T_d$  local ion symmetry). This line can be identified with the weak, strongly broadened band peaking near  $150\text{ cm}^{-1}$  ( $360\text{ K}$ ). The

shift of its frequency compared to the spectrum of  $\text{Rb}_2\text{KScF}_6$  correlates well with the change in the ion mass. Moreover, one also observes a broad wing of the central peak, which is evidently associated with the strong disorder in the cubic-phase structure.

Lowering the temperature down to the transition point to the monoclinic phase brings about considerable changes in this part of the spectrum. The widths of all lines decrease strongly, which is accompanied by an increase in their frequency (Fig. 4). A new line, seen clearly in Fig. 3, appears against the background of the low-frequency wing.

All these changes occur in a jump, within a  $1\text{--}2\text{ K}$  interval, with no further modification of the spectrum being observed within the region of existence of the monoclinic phase. This correlates well with the first-order nature of this phase transition, although no noticeable hysteresis effects were revealed.

The strong broadening of the lines corresponding to the internal vibrations of the  $\text{ScF}_6^{3+}$  ions and to the  $(\text{NH}_4)\text{II}$  sublattice vibration in the cubic phase implies that they are also disordered. It is apparently the heavier  $\text{ScF}_6^{3+}$  ions that also primarily govern the nature of the

broad low-frequency wing. The strong narrowing and the spectral-line shift to a higher frequency support the conjecture that the transition from the cubic to the monoclinic phase is associated with the ordering processes while the main ordering structural unit is the  $\text{ScF}_6^{3+}$  ions and, therefore, their internal modes are the most strongly modified. The ordering of the  $\text{ScF}_6^{3+}$  sublattice makes the potential relief of the structure as a whole more pronounced, and, as a result, the ammonium group vibrations are also modified, although to a lesser extent, whereas the internal vibrations of the ammonium ions remain strongly broadened. The extremely strong broadening of these modes makes it difficult to determine which of the ammonium sublattices is more disordered, however, the substantial change in the parameters of the lattice-phonon line at  $150\text{ cm}^{-1}$  suggests that the  $(\text{NH}_4)II$  sublattice plays no less a part than the  $(\text{NH}_4)I$  sublattice in this transition. Judging from the appreciable widths of the internal vibrations of both ammonium sublattices, these sublattices also remain disordered in the monoclinic phase and their ordering may turn out to be a dominant factor in the mechanisms of lower temperature phase transitions.

## ACKNOWLEDGMENTS

The authors express sincere gratitude to K.S. Aleksandrov and I.N. Flerov for the samples and fruitful discussions.

This study was supported by the INTAS Program (grant no. 97-10177), Russian Foundation for Basic Research (project no. 00-02-16034), and Integration Program of the Siberian Division of the RAS.

## REFERENCES

1. K. S. Aleksandrov and B. V. Beznosikov, *Perovskite-like Crystals* (Sib. Otd. Ross. Akad. Nauk, Novosibirsk, 1999).
2. S. V. Mel'nikov, S. V. Misyul', A. F. Bovina, and M. L. Afanas'ev, *Fiz. Tverd. Tela* (St. Petersburg) **42** (2), 336 (2000) [*Phys. Solid State* **42**, 345 (2000)].
3. I. N. Flerov, M. V. Gorev, and T. V. Ushakova, *Fiz. Tverd. Tela* (St. Petersburg) **41** (3), 523 (1999) [*Phys. Solid State* **41**, 468 (1999)].
4. K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds* (Wiley, New York, 1963; Mir, Moscow, 1966).
5. M. Cousi, S. Khairoun, and A. Tressaud, *Phys. Status Solidi A* **98** (1), 423 (1986).

*Translated by G. Skrebtsov*