

Raman spectra and pressure-induced lattice instabilities in RbMnCl₃ crystal

A. N. Vtyurin^{*1}, S. V. Goryainov², A. S. Krylov¹, S. N. Krylova¹, A. D. Shefer¹, N. G. Zamkova¹, and V. I. Zinenko¹

¹ Kirensky Institute of Physics, 660036 Krasnoyarsk, Russia

² Institute of Mineralogy and Petrography, 630090 Novosibirsk, Russia

Received 12 July 2004, revised 19 August 2004, accepted 6 September 2004

Published online 17 November 2004

PACS 63.20.Dj, 64.70.Kb, 77.84.Bw, 78.30.Hv

Raman scattering spectra of the RbMnCl₃ crystal have been studied under ambient conditions and under high hydrostatic pressure. The results produced have been interpreted with the *ab initio* model. The experimental data agree well with the estimated values in the low frequency range and show a slightly worse agreement at higher frequencies. A phase transition from the hexagonal phase to the perovskite phase predicted earlier within the same model was observed under high pressure (above 0.7 GPa) and new transitions to lower symmetry phases were found at higher pressures (1.1 GPa and 5 GPa).

© 2004 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

1 Introduction The RbMnCl₃ crystal belongs to a big perovskite-like family of ABX₃ structures built of rigid BX₆ octahedrons. Connected by apical anions they form classical cubic lattices. Such lattices are widely known and well studied for oxygen systems. Edge-joined, the octahedrons produce a hexagonal lattice. Halogen-containing perovskites are known to be in cubic and hexagonal modifications and may also form mixed layered structures.

RbMnHal₃ crystals feature all types of those structures. Under ambient conditions RbMnF₃ is a cubic perovskite, RbMnBr₃ forms a “standard” hexagonal structure, and RbMnCl₃ is an example of a mixed six-layer system [1, 2]. Similarity of chemical compositions and structures of these crystals suggests a phase transition between these structures induced by changes in external conditions which brings forth sharp anomalies in the lattice dynamics. Indeed, under cooling the RbMnCl₃ crystal was observed to transit to a lower symmetry phase [3] and under a combination of high temperature and high pressure – to a cubic phase [4, 5].

Recent theoretical studies of this group of crystals [6] by the *ab initio* approach [7] have shown that under high pressure (without heating) the hexagonal RbMnCl₃ tends to turn unstable, and the cubic modification becomes predominant (the estimated transition pressure is just above 1 GPa). However, the calculated difference in the energies of these competitive phases is negligible and strongly depends on the fine balance of higher multipole-multipole interactions of their structural units. Therefore, both the validity of this simulation approach for these particular crystals and the existence of the predicted transition should be checked experimentally. To address this problem, this paper studies the Raman spectra of the RbMnCl₃ crystal under ambient conditions, compares them with the simulation results obtained within the same model [7] and by a very similar approach [8] and investigates the Raman spectra behavior under applied hydrostatic pressure.

* Corresponding author: e-mail: vtyurin@iph.krasn.ru, Phone: +7 3912-494294, Fax: +7 3912 438923

2 Samples, structure and symmetry Bulk red single crystals of 40 mm diameter and 50 mm length were grown in quartz ampoules by the Bridgeman method. Samples for polarized Raman spectroscopy experiments were prepared as 3×4×5 mm³ parallelepipeds with two edges parallel (within ±15°) to the *a* and *c* axes of the hexagonal structure. The technique of crystal growing and sample preparation is described in [3] in more detail.

Under ambient conditions the crystal belongs to the *P6₃/mmc* space group, *Z* = 6 [1, 9]. Vibrational representation at the center of Brillouin zone is

$$\Gamma = 5A_{1g}(xx, yy, zz) + 6E_{1g}(xz, yz, zx, zy) + 8E_{2g}(xx, yy, xy, yx) + A_{1u} + 7A_{2u} + 2B_{1u} + 6B_{2u} + 9E_{1u} + 7E_{2u} + 2A_{2g} + 6B_{1g} + B_{2g}, \quad (1)$$

where respective components of the Raman scattering tensor are given in brackets. This representation for the cubic phase has form

$$\Gamma = 4F_{1u} + F_{2u}. \quad (2)$$

There are no active Raman representations here. From Eq. (2) it is apparent that the selection rules for these phases are considerably different; this makes their diagnosis by Raman scattering quite obvious.

3 Experimental techniques and results Experiments under ambient conditions were carried out with a modified DFS-24 double-grating Raman spectrometer and a 514.5 mm 0.5 W Ar⁺ laser excitation. A detailed description of the experimental arrangement and data processing procedure can be found in [10]. The experimental spectra in four different scattering geometries are shown in Fig. 1. The respective vibrational representations are (1): $y(xx)z - 5A_{1g} + 8E_{2g}$, $y(xy)z - 8E_{2g}$, $y(xz)x - 6E_{1g}$, $y(zz)x - 5A_{1g}$.

The frequencies of the lattice modes obtained are given in Table 1. The spectra have been analyzed in detail in [11].

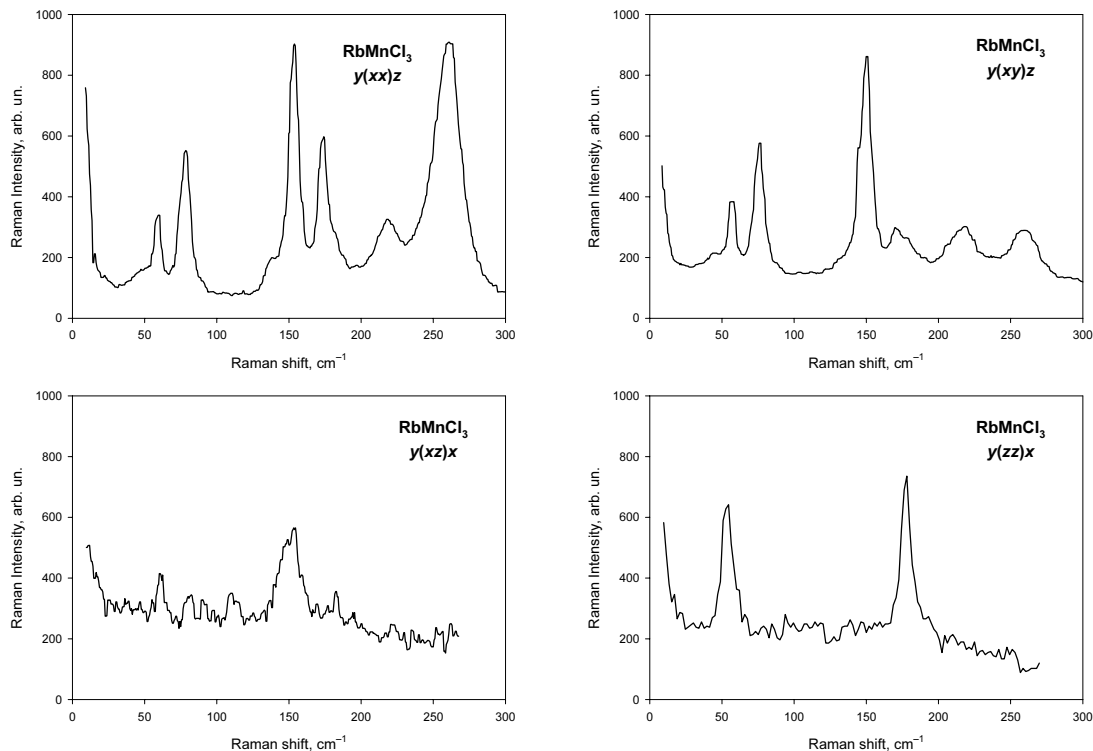


Fig. 1 Polarized Raman spectra of RbMnCl₃ crystal under ambient conditions.

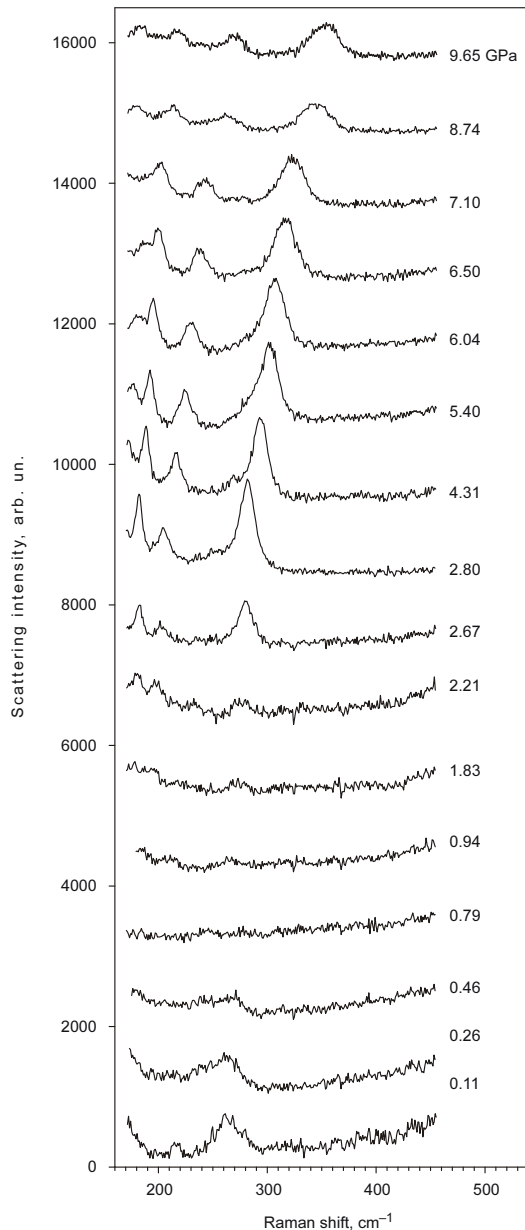


Fig. 2 Transformation of the upper part of Raman spectra of RbMnCl_3 crystal under hydrostatic pressure.

The experiments under hydrostatic pressure were performed in a diamond anvil cell as in [12–14]. The pressure was measured by the ruby luminescent shift with an accuracy of 0.05 GPa. The Raman spectra were obtained with OMARS 89 (Dilor) spectrometer and Ar^+ laser (514.5 nm, 0.5 W) excitation. Because of the small ($< 70 \mu\text{m}$) size of the samples and strong diffuse scattering only the higher-frequency part of the spectra was measured. Transformations of the samples were concurrently observed under a polarizing microscope.

Figure 2 shows the transformation of the spectrum. At the ambient pressure the familiar intense peak is observed at 260 cm^{-1} , a weak maximum – at 218 cm^{-1} and a wing of the $154 \text{ cm}^{-1} - 174 \text{ cm}^{-1}$ doublet. The picture does not change (but for a minor shift towards higher frequencies) up to approx. 0.4 GPa, where the lines' intensity starts decreasing. At the same time, optically isotropic regions were observed under the microscope. It should be noted that the possibility of hexagonal and cubic phases to separate was reported in [5]. The spectrum disappears completely above 0.75 GPa and the sample becomes optically isotropic (except for a few smaller regions at the surface). This transition point agrees well with 1.1 GPa predicted in [6] and with 0.7 GPa found in [4] at high temperatures.

Under further compression, the spectrum reappears at approx. 1.1 GPa but now its shape is different. The line at 218 cm^{-1} disappears whereas a new doublet is observed at 200 cm^{-1} . The intensities of these lines keep growing as they drift up continuously. At 5 GPa, the drift runs faster and the intensities start dropping, which is supposedly caused by yet another phase transformation.

Nothing new happens up to 9.65 GPa. When decompressed, the sample follows the same sequence of transformations back to the initial state. Repeated transitions from the hexagonal phase to the cubic one and back do not cause any shift of transition points (within our precision) and no hysteresis effects were observed either (unlike [4] where the annealed cubic phase remained after decompression).

4 Results and discussion The spectra obtained have been compared with the results of numerical simulations reported in [7, 11] and [8]. Both approaches are based on a modified *ab initio* Gordon-Kim model: in [7, 11] it was expanded to take into account ionic multipole moments and in [8] it was used to estimate the parameters of the rigid charge model potential. To attribute the experimental lines to the calculated modes, a symmetry analysis [11] was used. The results are given in Table 1.

Table 1 Experimental and calculated frequencies (cm⁻¹) of Raman lines in hexagonal phase of RbMnCl₃.

Ir. Rep.:	A _{1g}	A _{1g}	A _{1g}	A _{1g}	A _{1g}	E _{1g}	E _{1g}	E _{1g}	E _{1g}	E _{1g}	E _{1g}	E _{2g}	E _{2g}	E _{2g}	E _{2g}	E _{2g}	E _{2g}	E _{2g}	E _{2g}
Calc. [11]:	52	90	114	149	189	25	53	69	97	155	65i	24	42	53	76	90	105	157	67i
Calc. [8]:	40	161	254	339	368	44	120	157	171	301	51i	39	55	80	143	216	242	306	39i
Experiment:	55		138	178	260		55	80?	111	153			49	60	78	154	174	218	

The agreement appears to be rather good for the *ab initio* simulations. Several imaginary frequencies exhibited instability of the hexagonal lattice at 0 K, which agrees with the lower temperature phase transition [3]; this instability was discussed in detail in [8]. According to the experiment, the highest frequency calculated phonons correspond to the A_{1g} mode connected with the longitudinal Mn–Cl vibrations (also see [11]).

It should be noted that both approaches [7] and [8] yield qualitatively similar distributions of phonons over the spectrum and they are in good quantitative agreement with the experimental data in the middle of the frequency range. However, at higher frequencies their disagreement becomes considerable. Analysis of the high-frequency phonons' eigenvectors [11] shows that they are mainly connected with the longitudinal Mn–Cl vibrations. The rigid charges potential seems to overestimate considerably the corresponding force constants while the multipole approach somewhat underestimates them.

The pressure value for the transition from the hexagonal phase to the cubic phase (0.7 GPa) is in reasonable agreement with the estimated value (1.1 GPa). The observed optical isotropy of this high-pressure phase is quite consistent with its cubic symmetry.

5 Conclusion Thus, we can conclude that the *ab initio* approach provides an effective tool to simulate the lattice stability and dynamics for ionic crystals of a rather complex structure. Some disagreement with the experiment observed at higher frequencies is probably due to the partial covalence of the Mn–Cl bonds.

A transition from the hexagonal to the cubic phase has been observed in RbMnCl₃ for the first time under high pressure at room temperature; the transition pressure is in good agreement with the predicted value. New transitions have also been found at 1.1 GPa and at 5 GPa.

Acknowledgements Helpful discussions with Professor K. S. Aleksandrov are gratefully acknowledged. One of the authors (A. S. K.) would like to thank Russian Science Support Foundation, and the other (S. V. G.) – RFBR (grant 02-05-65313) and CRDF-BRHE (grant NO-008-X1), for financial support.

References

- [1] K. S. Aleksandrov et al., Phase Transitions in Crystals of Haloid Compounds (Nauka, Novosibirsk, 1981).
- [2] K. S. Aleksandrov and B. V. Beznosikov, Perovskite-Like Crystals (Nauka, Novosibirsk, 1997).
- [3] K. S. Aleksandrov, A. T. Anistratov, S. V. Melnikova, V. I. Zinenko, L. A. Shabanova, and A. D. Shaffer, Phys. Solid State **21**, 1119 (1979).
- [4] J. M. Longo and J. A. Rafatas, J. Solid State Chem. **3**, 429 (1971).
- [5] I. P. Aleksandrova, V. F. Shabanov, A. K. Moskalev et al., Structural Phase Transitions in Crystals under High Pressure (Nauka, Novosibirsk, 1982).
- [6] V. I. Zinenko, N. G. Zamkova, and S. N. Sofronova, J. Exp. Theor. Phys. **96**, 747 (2003).
- [7] V. I. Zinenko, N. G. Zamkova, and S. N. Sofronova, J. Exp. Theor. Phys. **87**, 944 (1998).
- [8] M. B. Smirnov and V. Y. Kazimirov, Crystallogr. Rep. **48**, 435 (2003).
- [9] J. Goodyear, G. A. Steigmann, and E. M. Ali, Acta Crystallogr. B **33**, 256 (1977).
- [10] A. S. Krylov, A. D. Shaffer, and A. N. Vtyurin, Instrum. Exp. Tech. **38**, 386 (1995).
- [11] A. N. Vtyurin, S. V. Goryainov, N. G. Zamkova, V. I. Zinenko, A. S. Krylov, S. N. Krylova, and A. D. Shefer, Phys. Solid State **46**, 1301 (2004).
- [12] Q. Wang, G. Ripault, and A. Bulou, Phase Transitions **53**, 1 (1995).
- [13] S. V. Goryainov and I. A. Belitsky, Phys. Chem. Minerals **22**, 443 (1995).
- [14] R. G. Munro, G. J. Piermarini, S. Block, and W. B. Holzapfel, J. Appl. Phys. **57**, 165 (1985).