



# Isotope effect in $\text{Cs}_5\text{H}_3(\text{SO}_4)_4 \cdot 0.5\text{H}_2\text{O}$ crystals

Authors: S.G. Lushnikov, A.V. Belushkin, A.I. Beskrovnyi, A.I. Fedoseev, S.N. Gvasaliya, L.A. Shuvalov, and V. Hugo Schmidt

NOTICE: this is the author's version of a work that was accepted for publication in Solid State Ionics. Changes resulting from the publishing process, such as peer review, editing, corrections, structural formatting, and other quality control mechanisms may not be reflected in this document. Changes may have been made to this work since it was submitted for publication. A definitive version was subsequently published in [Solid State Ionics](#), [VOL # 125, ISSUES # 1-4, (October 1999)] DOI# [10.1016/S0167-2738\(99\)00165-4](https://doi.org/10.1016/S0167-2738(99)00165-4)

S.G. Lushnikov, A.V. Belushkin, A.I. Beskrovnyi, A.I. Fedoseev, S.N. Gvasaliya, L.A. Shuvalov, and V.H. Schmidt, "Isotope effect in  $\text{Cs}_5\text{H}_3(\text{SO}_4)_4 \cdot 0.5\text{H}_2\text{O}$  crystals," Solid State Ionics 125, 119-123 (October 1999). [http://dx.doi.org/10.1016/S0167-2738\(99\)00165-4](http://dx.doi.org/10.1016/S0167-2738(99)00165-4)

Made available through Montana State University's [ScholarWorks](http://scholarworks.montana.edu)  
[scholarworks.montana.edu](http://scholarworks.montana.edu)

# Isotope effect in $\text{Cs}_5\text{H}_3(\text{SO}_4)_4 \cdot 0.5\text{H}_2\text{O}$ crystals

S.G. Lushnikov<sup>a,\*</sup>, A.V. Belushkin<sup>b</sup>, A.I. Beskrovnyi<sup>b</sup>, A.I. Fedoseev<sup>a</sup>, S.N. Gvasaliya<sup>a</sup>,  
L.A. Shuvalov<sup>c</sup>, V.H. Schmidt<sup>d</sup>

<sup>a</sup>*A.F.Ioffe Physical Technical Institute RAS, 194021 St. Petersburg, Russia*

<sup>b</sup>*Frank Laboratory of Neutron Physics, JINR, 141980 Dubna, Russia*

<sup>c</sup>*Institute of Crystallography RAS, 117333 Moscow, Russia*

<sup>d</sup>*Physics Department, Montana State University, Bozeman, MT 59717, USA*

---

## Abstract

The sequence of phase transitions at temperatures from 290 to 420 K in the crystals of  $\text{Cs}_5\text{H}_3(\text{SO}_4)_4 \cdot 0.5\text{H}_2\text{O}$  (CTSM) and  $\text{Cs}_5\text{D}_3(\text{SO}_4)_4 \cdot 0.5\text{D}_2\text{O}$  (DCTSM) was studied by Brillouin light scattering and neutron diffraction. Anomalies in the temperature dependences of the velocity and damping of hypersonic acoustic phonons in the vicinity of 360 K were observed in the CTSM crystal. In contrast, no anomalies were found in the DCTSM crystal. Preliminary analysis of neutron diffraction data does not show symmetry changes in the temperature range studied. Thus it has been found that deuteration of the CTSM crystals leads to a change in the sequence of phase transitions. © 1999 Published by Elsevier Science B.V. All rights reserved.

*Keywords:* Superprotonic; Isotope effect; Brillouin scattering

---

## 1. Introduction

This work describes studies of high temperature phase transitions in crystals of  $\text{Cs}_5\text{H}_3(\text{SO}_4)_4 \cdot 0.5\text{H}_2\text{O}$  (CTSM) and  $\text{Cs}_5\text{D}_3(\text{SO}_4)_4 \cdot 0.5\text{D}_2\text{O}$  (DCTSM) by Brillouin light scattering and neutron diffraction. These compounds are representatives of superprotonic crystals, which have a dynamically disordered network of partially occupied hydrogen bonds in the high-temperature phase [1,2]. The properties of CTSM crystals have been widely studied. For instance, their structure was analyzed by X-ray diffraction [1,3], the conductivity mechanism

was studied by dielectric measurements [1,4], neutron scattering [5] and NMR spectroscopy [6], and the vibration spectrum was investigated by Raman and Brillouin light scattering and inelastic neutron scattering in a wide temperature range [7–10]. Nevertheless, the sequence of phase transitions is still unclear. At room temperature the symmetry is  $P6_3/mmc$  and remains the same down to helium temperatures. There is a more complicated situation with the high-temperature region: from the superprotonic phase with the supposed space group  $P6/mmm$  at  $T_1 = 414$  K the crystal passes into an intermediate phase with unknown symmetry [1,3]. Studies of the dynamics of the crystalline lattice of CTSM by Raman and Brillouin light scattering have revealed specific features in the behavior of scattering spectra in the vicinity of 360 K [7,8,10] con-

sistent with the anomalies in the temperature dependences of the real part of the dielectric constant  $\epsilon'$  [4] and spin-spin proton relaxation time [6]. Thus, there is good reason to believe that at 360 K an order-disorder phase transition takes place in the CTSM crystal [10].

The goal of this work was to study the sequence of phase transitions in the temperature range from 420 to 300 K in CTSM and DCTSM crystals.

The CTSM and DCTSM crystals were grown by slow evaporation from water solution at room temperature. For the light scattering experiments, samples in the form of parallelepipeds were cut so that the hexagonal axis (which lies along a natural crystal rib) was perpendicular to the basal plane. The crystal orientation was determined by a polarizing microscope. The sample surfaces were polished to optical quality. The light source was a single-mode Ar<sup>+</sup> Spectra-Physics laser with  $\lambda = 514.5$  nm. The scattered light was analyzed by a three- and five-pas piezoscanning Fabry-Perot interferometer.

The error in measuring and determining temperatures was  $\pm 0.5$  K. The samples were heated from 295 to 420 K in a stepwise fashion and the data were collected automatically. The Brillouin spectra were obtained in the backscattering geometry. A detailed analysis of the behavior of Brillouin spectra with varying temperature in protonic CTSM crystals was given in [10]. Neutron diffraction experiments were carried out with the DN-2 diffractometer placed at the IBR-2 reactor (JINR, Dubna).

As mentioned above, in the vicinity of 360 K a phase transition is realized in CTSM crystals. Symmetry of the intermediate phase  $360 < T < 414$  K has not been determined. Based on the analysis of Raman and Brillouin spectra, different models of symmetry of the intermediate phase were proposed [7,10], the most probable among them is the isostructural phase transition as a result of which the  $P6_3/mmc$  symmetry is preserved. To check this idea, we carried out neutron diffraction experiments with powdered DCTSM compound. At room temperature diffraction data are well described in the framework of the model of structure [3] with the space group  $P6_3/mmc$  ( $a_h = 6.2412(9)$  Å,  $c_h = 29.6561(8)$  Å,  $V = 1000.5$  Å<sup>3</sup>,  $Z = 2$ ). Some differences between the unit cell parameters obtained from neutron and X-ray data are due to the fact that in our experiments

deuterated samples were used. Heating the samples to 380 K did not lead to significant changes in the diffraction pattern. Further increase of temperature to 420 K resulted in modification of the diffraction pattern. A preliminary analysis showed that the neutron diffraction data at 420 K are well described in the framework of the known model involving the coexistence of CsDSO<sub>4</sub> and Cs<sub>2</sub>SO<sub>4</sub> compounds. It can be supposed that at 420 K the solid-phase reaction resulting in formation of the heterophase system takes place. Thus neutron diffraction experiments did not reveal changes in the symmetry of the DCTSM compound in the vicinity of 360 K.

Because of the contradictions between the results obtained in the neutron diffraction experiments for the DCTSM sample and light scattering experiments for the CTSM crystal, it seemed reasonable to perform Brillouin scattering measurements on deuterated crystals. Fig. 1 (a,b) shows velocity of longitudinal acoustic phonons in Cs<sub>5</sub>H<sub>3</sub>(SO<sub>4</sub>)<sub>4</sub> · 0.5H<sub>2</sub>O and Cs<sub>5</sub>D<sub>3</sub>(SO<sub>4</sub>)<sub>4</sub> · 0.5D<sub>2</sub>O crystals in two orthogonal directions: along the hexagonal axis and in the basal plane. It is clearly seen that relative changes in the velocity of hypersonic phonons propagating in the basal plane are different for the deuterated and protonic crystals (Fig. 1a). Longitudinal phonons with  $\mathbf{q} \parallel [001]$  behave in a different fashion (Fig. 1b): the temperature dependences of their velocities in the crystals studied are similar. It should be noted that during the Brillouin experiments the contribution of elastic light scattering in protonic CTSM crystals in the vicinity of 360 K increased considerably and for this reason we could not perform the experiment above 360 K. This effect is absent in the light scattering experiments with deuterated CTSM crystals up to 420 K.

A more complicated situation is observed with the temperature dependence of a relative change in damping of hypersonic phonons (Fig. 2 a,b). It is well seen that relative changes in damping for protonic and deuterated CTSM crystals differ for both propagation directions under consideration. In the protonic crystal damping increases sharply in the vicinity of 360 K, while damping of hypersonic acoustic phonons in the deuterated crystal increases gradually to 420 K. The anomalous behavior of Brillouin scattering at phase transition in CTSM in the vicinity of 360 K was considered in detail in

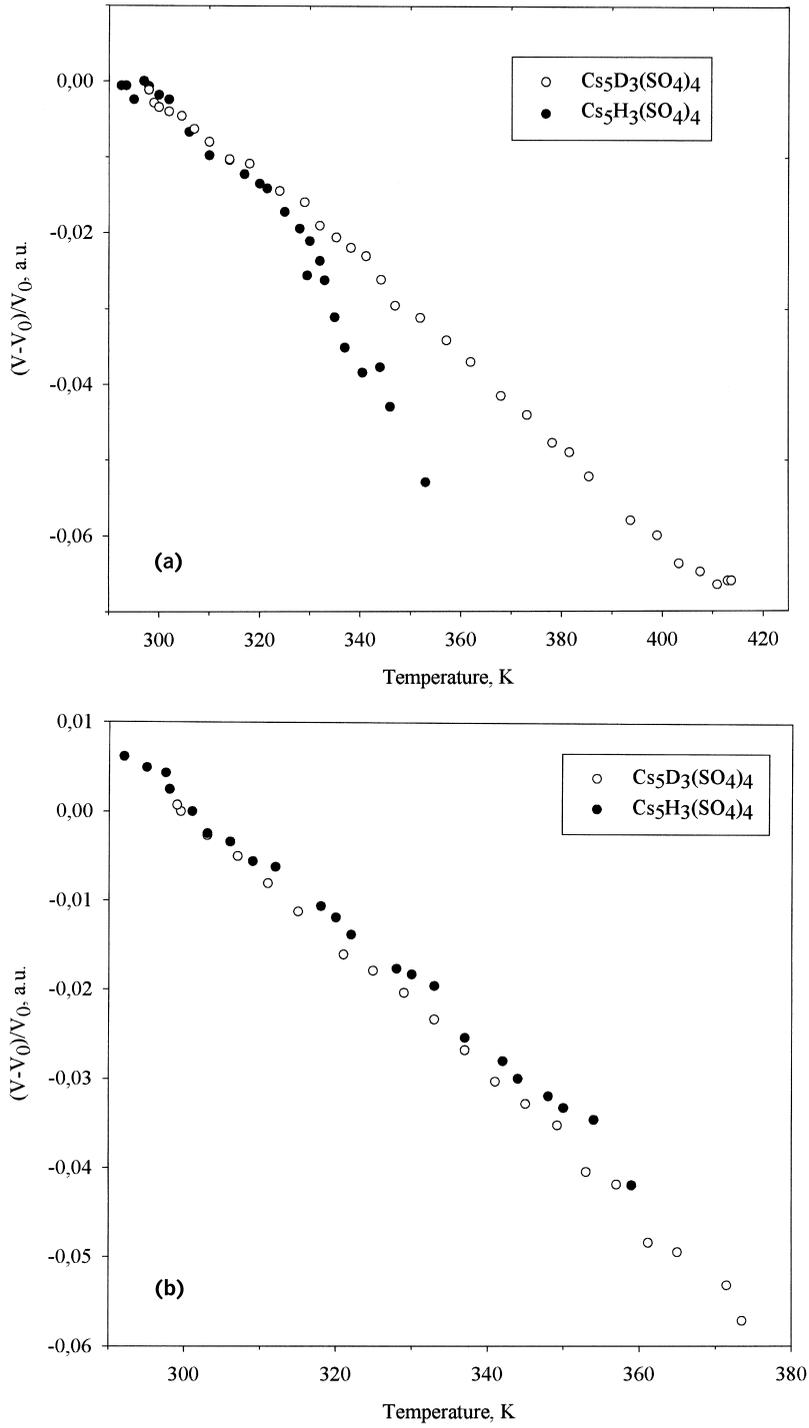


Fig. 1. (a) Temperature dependences of the relative changes in the velocity of hypersonic longitudinal phonons propagating in the basal plane for the deuterated and protonic CTSM crystals. (b) Temperature dependences of the relative changes in the velocity of hypersonic longitudinal phonons with  $q \parallel [001]$  for the deuterated and protonic CTSM crystals.

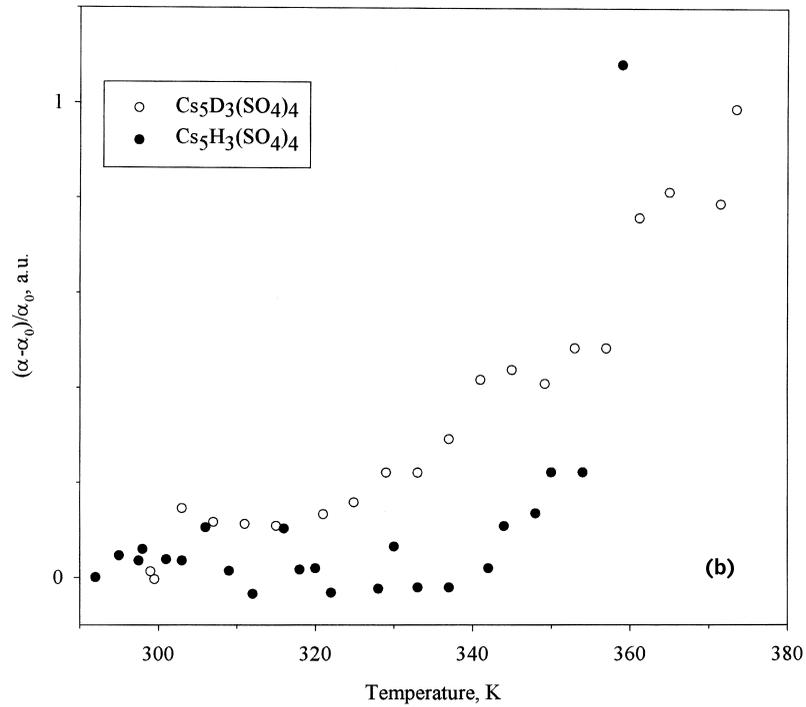
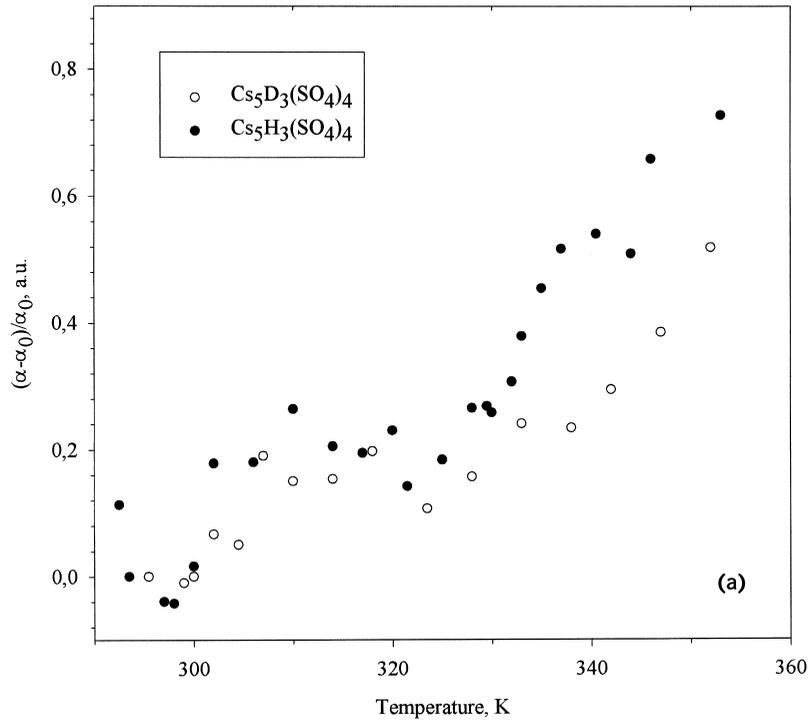


Fig. 2. (a) Temperature dependences of the relative changes in the damping of hypersonic longitudinal phonons propagating in the basal plane for the deuterated and protonic CTSM crystals. (b) Temperature dependences of the relative changes in the damping of hypersonic longitudinal phonons with  $q_{\parallel}[001]$  for the deuterated and protonic CTSM crystals.

[10]. Here we only note that a strong anisotropy in the hypersound damping corresponds to the quasi-two-dimensionality of superprotonic conductivity. On the contrary to CTSM, the DCTSM crystals are characterized by a similar damping behavior of acoustic phonons propagating in the basal plane and along the hexagonal axis. It follows from the facts given above that damping in DCTSM in the temperature range studied is mainly determined by the interaction between the dynamic network of hydrogen bonds and longitudinal acoustic phonons.

Thus the data given here show that the behavior of the deuterated CTSM crystal dramatically differs from that of its protonic analog: deuteration of CTSM crystals leads to disappearance of phase transition in the vicinity of 360 K, which should be regarded as a manifestation of the isotope effect.

### Acknowledgements

The authors wish to express their thanks to Mrs V.V. Dolbinina for sample preparation.

This work was supported in parts by RFBR Grants No. 96-02-17859 and 96-02-17754, and NSF Grant DMR-9520251.

### References

- [1] A.I. Baranov, O.A. Kabanov, B.V. Merinov, L.A. Shuvalov, *Ferroelectrics* 127 (1992) 257.
- [2] A.I. Baranov, O.A. Kabanov, L.A. Shuvalov, *JETP Lett.* 58 (1993) 548.
- [3] D.V. Merinov, A.I. Baranov, L.A. Shuvalov, J. Schneider, H. Schulz, *Solid State Ionics* 69 (1994) 153.
- [4] O.A. Kabanov, Ph.D. thesis, Institute of Crystallography, Moscow, 1993, (unpublished).
- [5] A.V. Belushkin, C.J. Carlile, L.A. Shuvalov, *Ferroelectrics* 167 (1995) 21.
- [6] A.M. Faidiga-Bulat, G. Lahajnar, J. Dolinsek, J. Slak, B. Lozar, B. Zalar, L.A. Shuvalov, R. Blinc, *Solid State Ionics* 77 (1995) 101.
- [7] Yu.I. Yuzyuk, V.P. Dmitriev, V.V. Loshkarev, L.M. Rabkin, L.A. Shuvalov, *Ferroelectrics* 167 (1995) 53.
- [8] Yu.I. Yuzyuk, V.P. Dmitriev, L.M. Rabkin, F. Smutny, I. Gregorat, V.V. Dolbinina, L.A. Shuvalov, *J.Phys. Condens Matter* 8 (1996) 3965.
- [9] A.V. Belushkin, M. Bull, C. Carlile, S.G. Lushnikov, L. Rosta, L.A. Shuvalov, D. Torok, B.T.M. Willis, *Physics B*, 1998, in press.
- [10] S.G. Lushnikov, V.H. Schmidt, L.A. Shuvalov, V.V. Dolbinina, submitted to *Phys. Rev. B*.