

# Raman scattering study of the upper phase transition in CsScF<sub>4</sub>

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Effects of the phase transition between the high-temperature tetragonal phases of the CsScF<sub>4</sub> crystal were studied by Raman scattering. The appearance of new lines including a soft mode was observed below the phase transition point, in complete accordance with the new crystal symmetry. The behavior of the soft mode, which corresponds to in-phase rotations of ScF<sub>6</sub> rigid groups around the z-axis (and out-of-phase within perovskite-like layers), resembles that observed earlier in RbAlF<sub>4</sub>, which suggests a similar mechanism of this transition in both crystals. Copyright © 2000 John Wiley & Sons, Ltd.

## INTRODUCTION

The CsScF<sub>4</sub> crystal presents a typical example of a layered perovskite structure. It is formed by square layers of ScF<sub>6</sub> octahedra connected via common F atoms (here called 'planar' fluorines), and separated with Cs<sup>+</sup> ions in interlayer holes (the fluorines that belong to a single octahedron are called 'axial'). According to x-ray data and macroscopic measurements,<sup>1</sup> the space group of its high-temperature phase is  $D_{4h}^1$ , the highest symmetry for such an arrangement. Cooling below 475 K results in a new phase with  $D_{4h}^5$  symmetry, in which the elementary cell volume is doubled. A second phase transition appears at 317 K leading to a phase with  $D_{2h}^{13}$  space group and a further doubling of the cell volume (the main characteristics of these lattices are given in Table 1).

Sc-containing layered perovskites have not been widely studied; such a phase sequence is also unusual for Cs-containing perovskites-like systems as well,<sup>2</sup> and is similar to that observed in RbAlF<sub>4</sub>.<sup>3</sup> Such transitions in the latter crystal clearly show a displacive character since soft-mode condensations were evidenced by Raman spectroscopy<sup>4,5</sup> and inelastic neutron scattering.<sup>6</sup> However, inelastic neutron scattering results and lattice dynamics simulations<sup>6</sup> also showed that the upper ( $D_{4h}^1$ – $D_{4h}^5$ ) transition is not just associated with the softening of a single phonon, but of a flat phonon branch. That gave a reason to propose for this transition a mechanism<sup>7</sup> where the displacive lattice distortion of the upper phase would induce a disordered state at a temperature  $T_L$  well above the temperature of the phase transition; hence the mechanism of the transition as macroscopically observed would be mainly order–disorder. This  $T_L$  temperature may be estimated from the behavior of the soft mode as measured

by Raman scattering below the actual phase transition. In RbAlF<sub>4</sub> such an estimation gave a  $T_L$  value not far from the melting point of the crystal, which made it difficult to put in evidence clearly the various effects expected for a change from an ordered to a disordered state (without any change in the crystal symmetry). The present study was intended to find whether CsScF<sub>4</sub> would be a more convenient system where these effects could be more clearly evidenced.

## EXPERIMENTAL

Samples for experiments, taken from the same crystallization as in Ref. 1, were selected under a polarizing microscope to minimize possible effects of crystal inhomogeneity due to ferroelastic domain structure, and cut ( $1 \times 3 \times 6$  mm<sup>3</sup>) along the crystallographic axes of the  $D_{4h}^5$  phase to obtain polarized Raman spectra. The crystals were transparent and colorless. The temperature during the experiment was fixed within 0.1 K. Spectra were excited by 514.5 nm, 0.5 W argon ion polarized laser radiation. They were obtained partly at 90° geometry with a U-1000 double-grating Raman spectrometer (spectral width 2 cm<sup>-1</sup>, scan step 1 cm<sup>-1</sup>), and partly under a microscope in backscattering geometry with a Dilor Z-24 triple monochromator (spectral width 3 cm<sup>-1</sup>, scan step 1 cm<sup>-1</sup>).

## SYMMETRY ANALYSIS AND EXPERIMENTAL RESULTS

The vibrational representation for the  $D_{4h}^1$  phase is

$$\Gamma = A_{1g} + E_g + 4A_{2u} + B_{2u} + 5E_u \quad (1)$$

where only the  $A_{1g}$  and  $E_g$  modes are Raman active. They correspond to vibrations of 'axial' fluorine atoms normally and in the octahedra sheets, respectively. For the  $D_{4h}^5$  phase one obtains

$$\Gamma = 2A_{1g} + 2A_{2g} + B_{1g} + B_{2g} + 3E_g + 2A_{1u} + 4A_{2u} + 2B_{1u} + 8E_u \quad (2)$$

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**Table 1. Symmetry and cell parameters for CsScF<sub>4</sub> crystal**

	Phase I	Phase II	Phase III
Space group	$D_{4h}^1$	$D_{4h}^5$	$D_{2h}^{13}$
Z	1	2	4
Cell parameters	$a_1$ $b_1 (b_1 = a_1)$ $c_1$	$a_2 = a_1 - b_1$ $b_2 = a_1 + b_1 (b_2 = a_2)$ $c_2 = c_1$	$a_3 = a_2 + b_2 = 2a_1$ $b_3 = -a_2 + b_2 = 2b_1$ $c_3 = c_2 = c_1$

Hence seven Raman-active modes are predicted ( $A_{1g}$ ,  $B_{1g}$ ,  $B_{2g}$  and  $E_g$  symmetries) and so the phase transition under investigation should result in the disappearance of some lines on heating the crystal above the transition point, mainly due to the Brillouin zone reconstruction so that some of them transform to the zone boundary<sup>4,6</sup> (M point). These modes involve vibrations of 'planar' and 'axial' fluorine atoms.<sup>6</sup>

An overview of the experimental spectra at 348 K is shown in Figs 1–3. This temperature was chosen for initial analysis since it is fairly far from the upper phase transition (well 'inside' the  $D_{4h}^5$  phase). The Raman shifts of the lines observed and their attributions are summarized in Table 2.

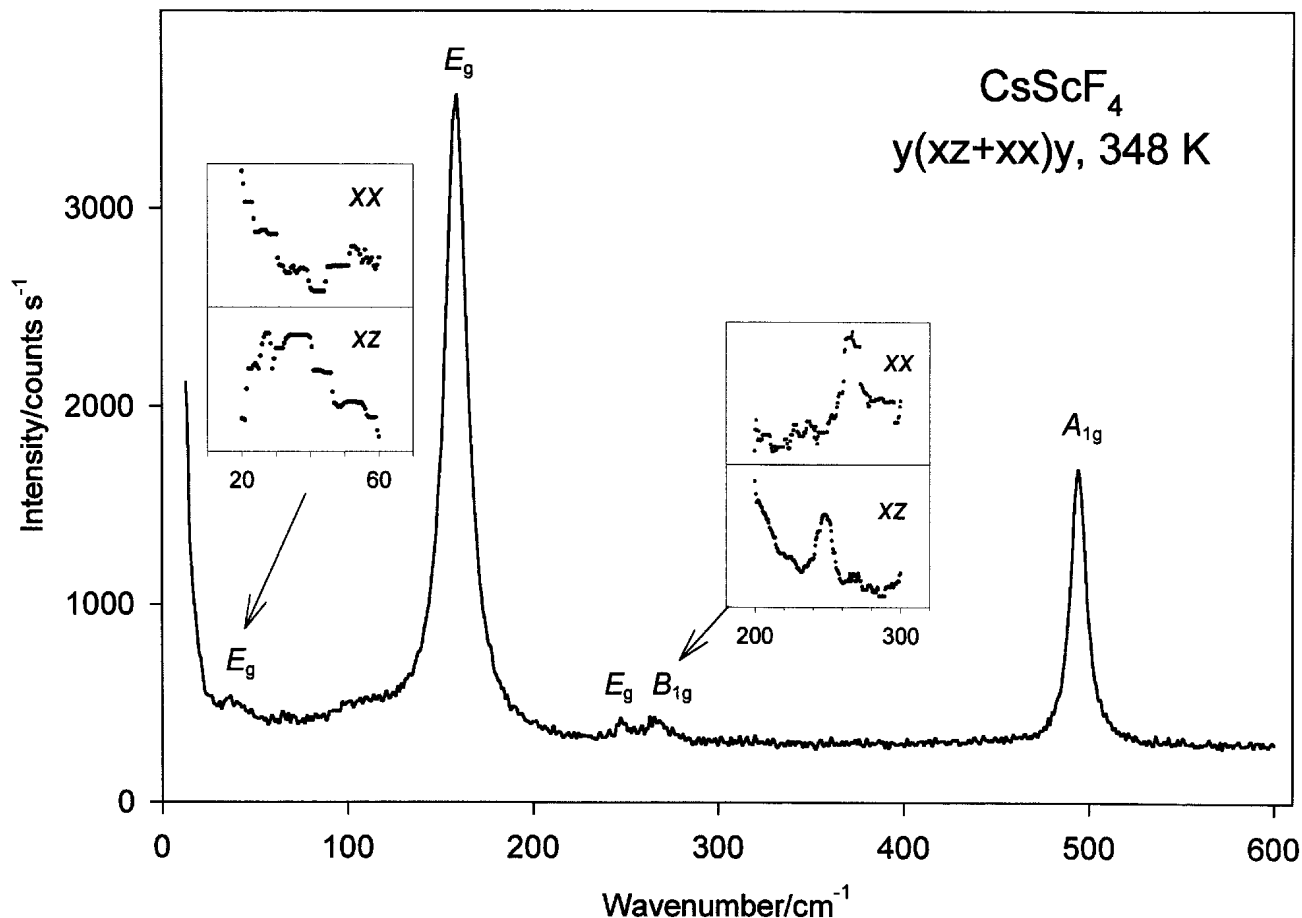
It should be noted that the present results bring new features with respect to the recently published analysis of the Raman spectra of the CsScF<sub>4</sub> second tetragonal phase.<sup>8</sup> Mainly it is due to the microRaman technique used in

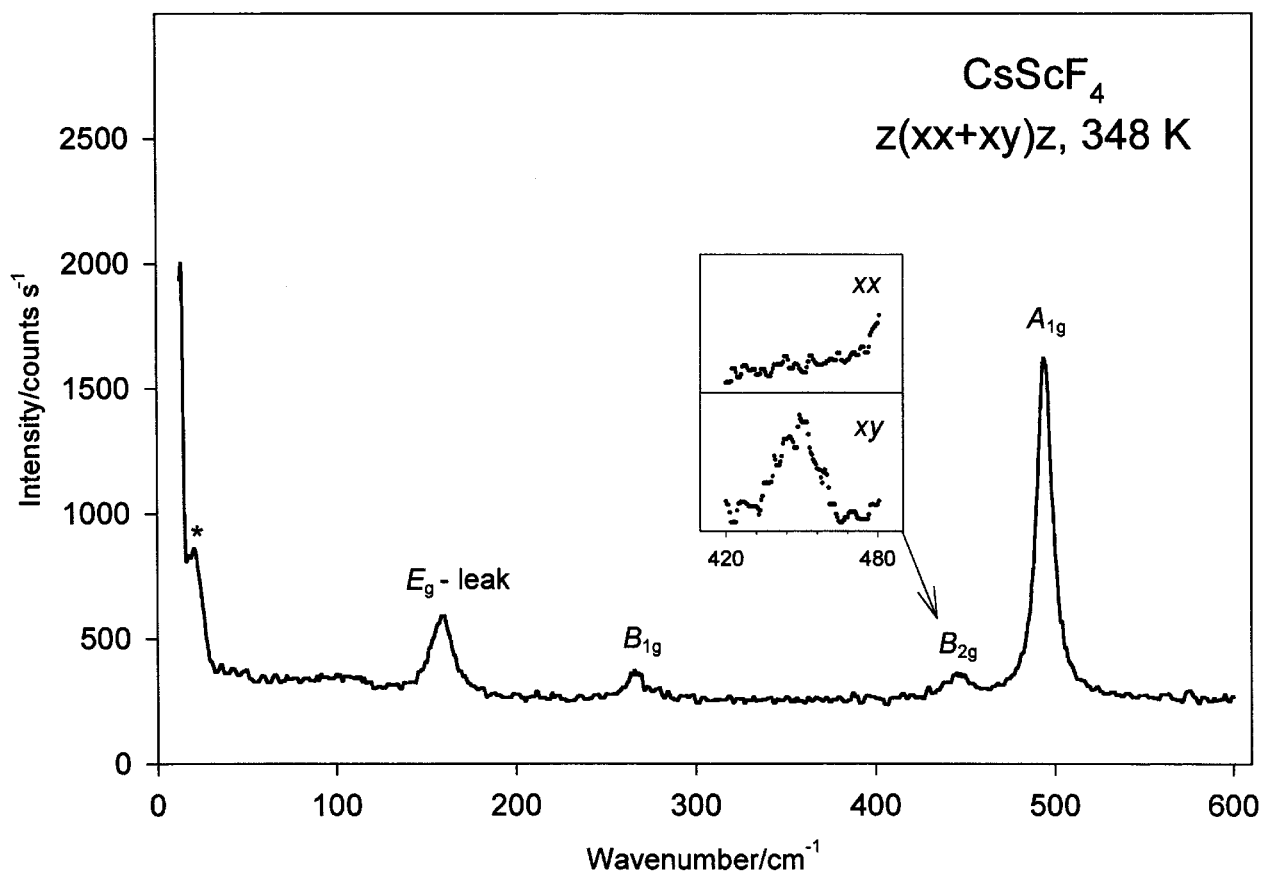
**Table 2. Wavenumbers ( $\tilde{\nu}$ ) and characteristics of Raman-active modes of CsScF<sub>4</sub> and their attribution in the  $D_{4h}^5$  phase ( $T = 348$  K)**

$\tilde{\nu}/\text{cm}^{-1}$	Intensity	Raman component	Irreducible representation
107	Medium	$xx, yy, zz$	$A_{1g}$
494	Strong		
266	Medium	$xx, yy$	$B_{1g}$
446	Medium	$xy$	$B_{2g}$
32	Medium	$yz, xz$	$E_g$
158	Very strong		
248	Medium		

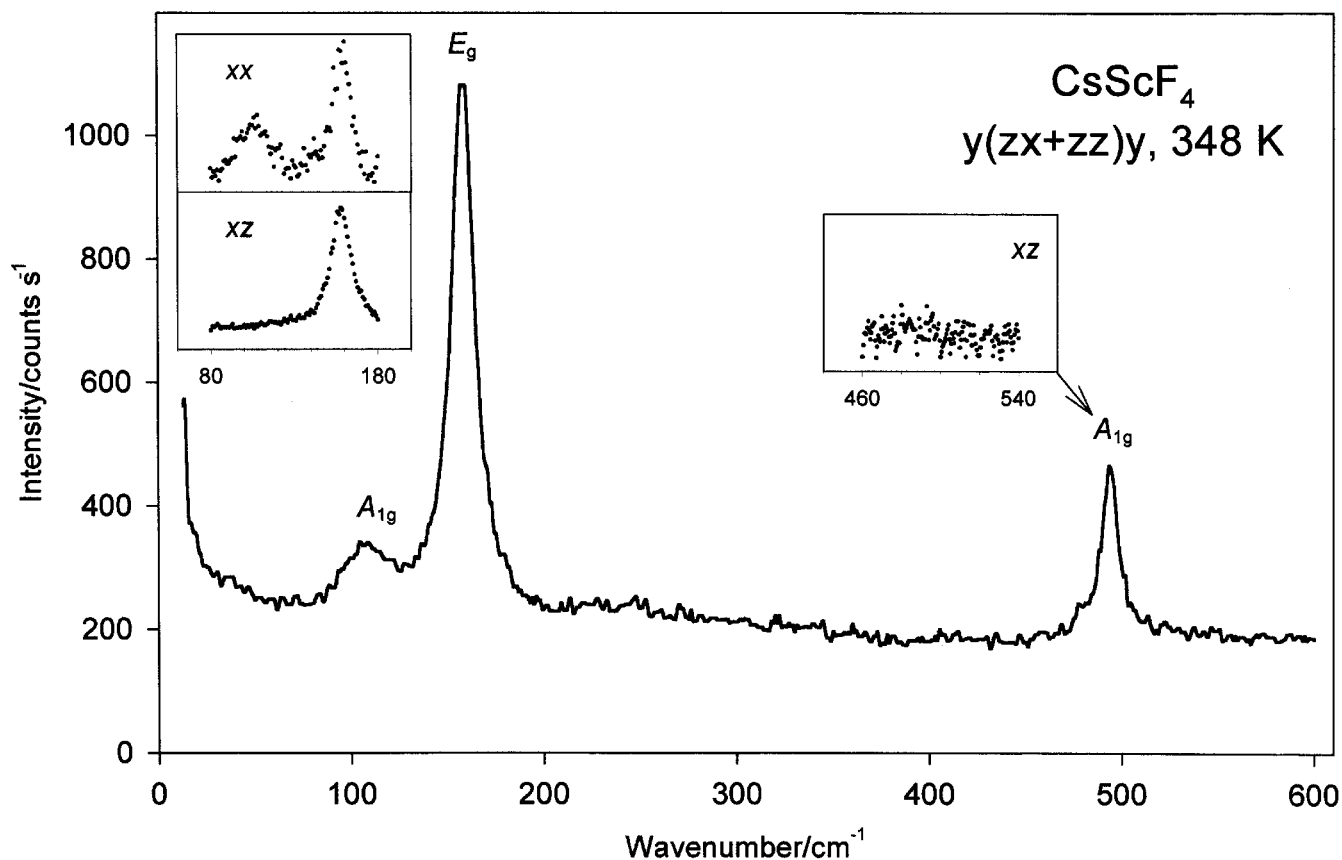
this study, which allows one to choose the best defectless parts of the sample, improves the signal-to-noise ratio and helps to avoid elastic light scattering from defects and intercomponent leaks of spectral lines that were mentioned earlier.<sup>8</sup> The only leak we failed to avoid completely is from the strongest  $E_g$  line at  $158 \text{ cm}^{-1}$ , which appears slightly in the  $xx$  component also. Still this minor leak is about an order of magnitude less than the intensity of this line in the  $xz$  component and may be attributed easily to the scattering on the sample domain structure.

Sample heating results in a continuous decrease of the lines marked in Table 2 as medium, with only slight changes in their wavenumbers. The only exception is the line at  $107 \text{ cm}^{-1}$ , which dramatically softens on heating (Fig. 4; the  $E_g$  line at  $158 \text{ cm}^{-1}$  is shown there as a

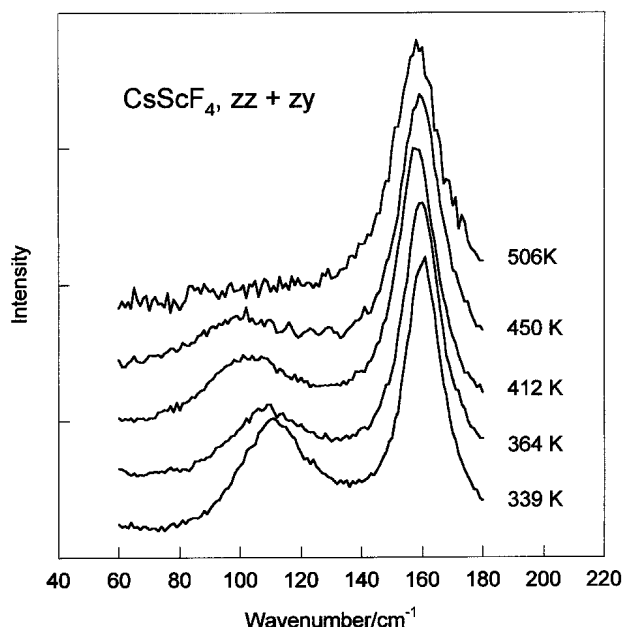
**Figure 1.** Overview of CsScF<sub>4</sub> Raman spectra.  $T = 348$  K,  $y(xz)y$  and  $y(xx)y$  Raman components.



**Figure 2.** Overview of CsScF<sub>4</sub> Raman spectra.  $T = 348$  K,  $z(xx)z$  and  $z(xy)z$  Raman components. Plasma discharge line is marked with an asterisk.



**Figure 3.** Overview of CsScF<sub>4</sub> Raman spectra.  $T = 348$  K,  $y(zx)y$  and  $y(zz)y$  Raman components.

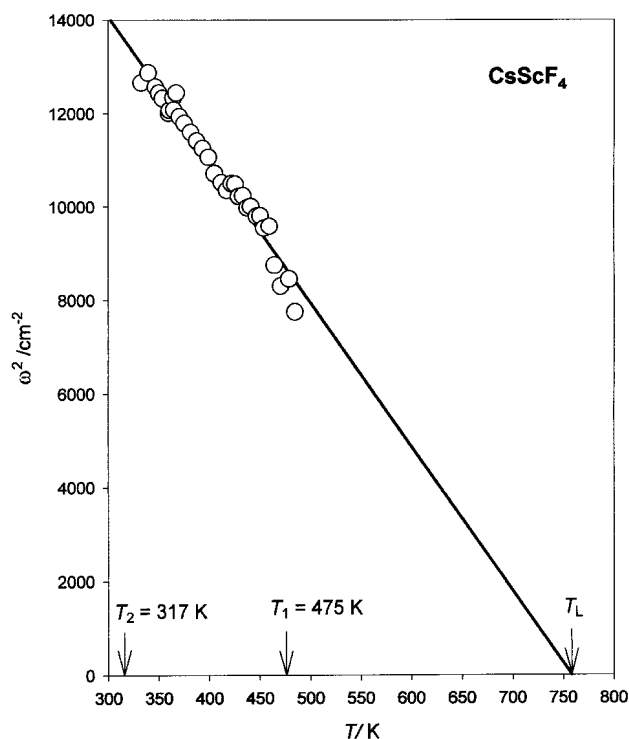


**Figure 4.** Temperature dependence of Raman-active soft mode in the lower tetragonal phase of CsScF<sub>4</sub>.

reference). Its intensity drops continuously on heating, whereas the width remains constant within experimental error (about 1 cm<sup>-1</sup>). Heating above the phase transition point results in the disappearance of all lines except those at 494 cm<sup>-1</sup> (*A*<sub>1g</sub>) and 158 cm<sup>-1</sup> (*E*<sub>g</sub>), hence they are unambiguously attributed to the vibrations of the 'axial' fluorines alone.

## DISCUSSION

The most drastic result observed is the condensation of the full symmetry mode, shown in Fig. 4. The temperature dependence of the square of its wavenumber is shown in Fig. 5, and is almost linear. The wider spread of the experimental points at high temperature is due to the lower intensity of the line and higher noise of the experimental spectra (see Fig. 4). The experimental points have been approximated (by the least-squares method) to a linear temperature dependence and fit it fairly well over all the *D*<sub>4h</sub><sup>5</sup> phase without saturation at lower temperatures down to the second phase transition at *T*<sub>2</sub> = 317 K, where this wavenumber reaches 113 cm<sup>-1</sup>. At the same time, extrapolation of this dependence to zero wavenumber gives *T*<sub>L</sub> ≈ 770 K, which is much higher than the transition point *T*<sub>1</sub> = 475 K where macroscopic breaking occurs;<sup>1</sup> the latter agrees well with the disappearance of lines that we observed. Hence in spite of the continuous reconstruction of the crystal dynamics and hence the structure over all the *D*<sub>4h</sub><sup>5</sup> phase, and the rather small (within a few kelvin) hysteresis effects,<sup>1</sup> an important discontinuity of the soft-mode wavenumber occurs at the transition, which together with the considerable *T*<sub>L</sub> - *T*<sub>1</sub> difference gives a marked first-order character to it (although the crystal symmetry allows second order for this transition). As was shown by symmetry analysis,<sup>4,6,8</sup> there exists only one mode of *M*<sub>3</sub> symmetry that could induce such a change of crystal symmetry. Its eigenvector corresponds to rotations of



**Figure 5.** Temperature dependence of the square of the wavenumber of the soft mode.

rigid ScF<sub>6</sub> groups around the *z*-axis, in-phase along this axis and out-of-phase within perovskite-like layers. Such a temperature dependence of this mode resembles very much that obtained for the *D*<sub>4h</sub><sup>1</sup>-*D*<sub>4h</sub><sup>5</sup> phase transition in RbAlF<sub>4</sub>.<sup>4</sup>

## CONCLUSION

These Raman experiments proved that the tetragonal-tetragonal phase transition in CsScF<sub>4</sub> is of first and close to second order, with a mode softening below the transition temperature. Distortion, which drives this transition, is due to in-phase rotations of rigid ScF<sub>6</sub> groups around the *z*-axis.

The combination of all typical features of this transition (same eigenvector of the soft mode, absence of its wavenumber saturation down the next transition, important discontinuity of this wavenumber at the transition point, which results in a considerable *T*<sub>L</sub> - *T*<sub>1</sub> difference, and absence of distinct hysteresis effects) resembles closely those obtained for the *D*<sub>4h</sub><sup>1</sup>-*D*<sub>4h</sub><sup>5</sup> phase transition in RbAlF<sub>4</sub>,<sup>4</sup> and suggests a similar mechanism for it, with a disordered state between the two temperatures.<sup>7</sup> The considerable difference between the estimated value *T*<sub>L</sub> ≈ 770 K and the melting point (well above 1100 K) of CsScF<sub>4</sub> makes this crystal a promising object for experimental investigations of this state.

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