Raman scattering study of the upper phase transition in CsScF$_4$

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Effects of the phase transition between the high-temperature tetragonal phases of the CsScF$_4$ 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$_6$ rigid groups around the z-axis (and out-of-phase within perovskite-like layers), resembles that observed earlier in RbAlF$_4$, which suggests a similar mechanism of this transition in both crystals. Copyright © 2000 John Wiley & Sons, Ltd.

INTRODUCTION

The CsScF$_4$ crystal presents a typical example of a layered perovskite structure. It is formed by square layers of ScF$_6$ octahedra connected via common F atoms (here called 'planar' fluorines), and separated with Cs$^+$ ions in interlayer holes (the fluorines that belong to a single octahedron are called 'axial'). According to x-ray data and macroscopic measurements,[1] 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,[2] and is similar to that observed in RbAlF$_4$.[3] Such transitions in the latter crystal clearly show a displacive character since soft-mode condensations were evidenced by Raman spectroscopy[4,5] and inelastic neutron scattering.[6] However, inelastic neutron scattering results and lattice dynamics simulations[6] 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[7] 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$_4$ 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$_4$ 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 $(1 \times 3 \times 6 \text{ mm}^3)$ 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^{-1}, scan step 1 cm^{-1}), and partly under a microscope in backscattering geometry with a Dilor Z-24 triple monochromator (spectral width 3 cm^{-1}, scan step 1 cm^{-1}).

SYMMETRY ANALYSIS AND EXPERIMENTAL RESULTS

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

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

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

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

Table 1. Symmetry and cell parameters for CsScF$_4$ crystal

	Phase I	Phase II	Phase III
Space group	D_{4h}^1	D_{4h}^5	D_{2h}^{13}
Z	1	2	4
Cell para-meters	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[4,6] (M point). These modes involve vibrations of 'planar' and 'axial' fluorine atoms.[6]

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$_4$ second tetragonal phase.[8] Mainly it is due to the microRaman technique used in

Table 2. Wavenumbers ($\tilde{v}$) and characteristics of Raman-active modes of CsScF$_4$ and their attribution in the D_{4h}^5 phase ($T = 348$ K)

$\tilde{v}$/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.[8] The only leak we failed to avoid completely is from the strongest E_g line at 158 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 cm^{-1}, which dramatically softens on heating (Fig. 4; the E_g line at 158 cm^{-1} is shown there as a
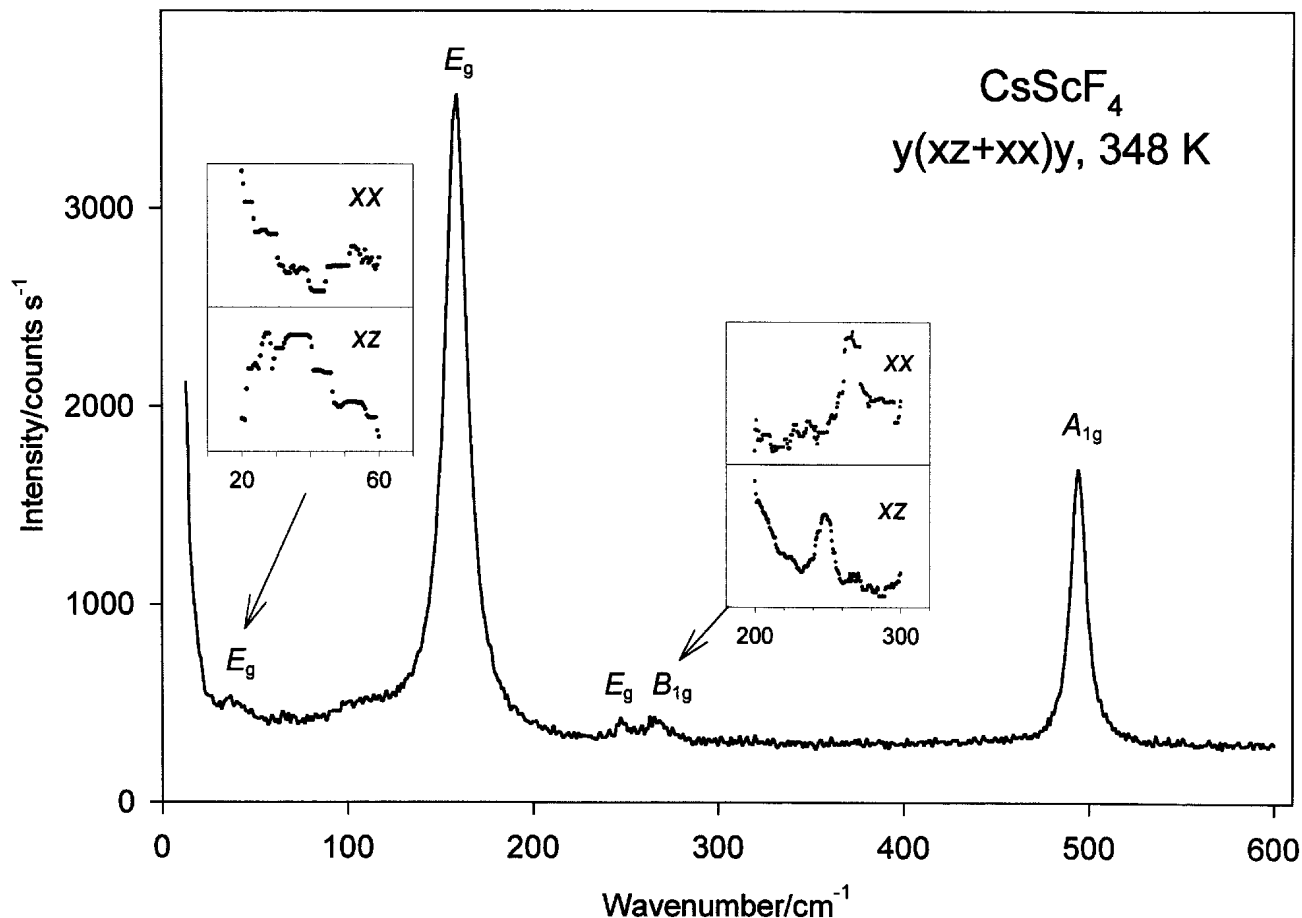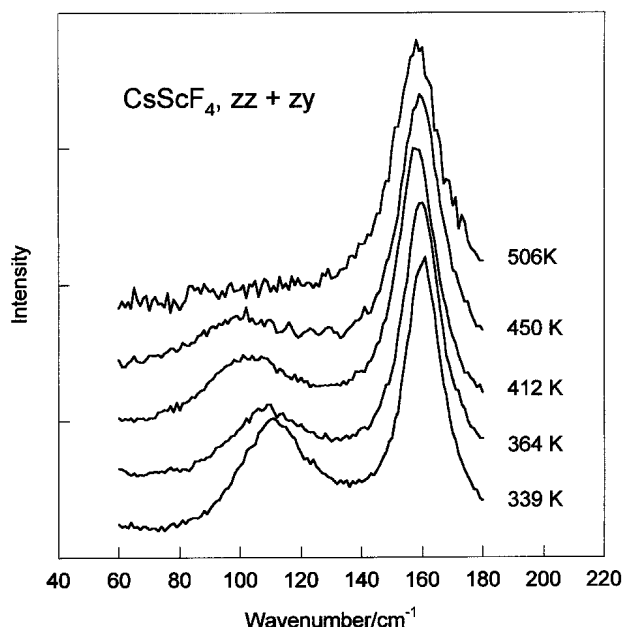

Figure 1. Overview of CsScF$_4$ Raman spectra. $T = 348$ K, $y(xz)y$ and $y(xx)y$ Raman components.
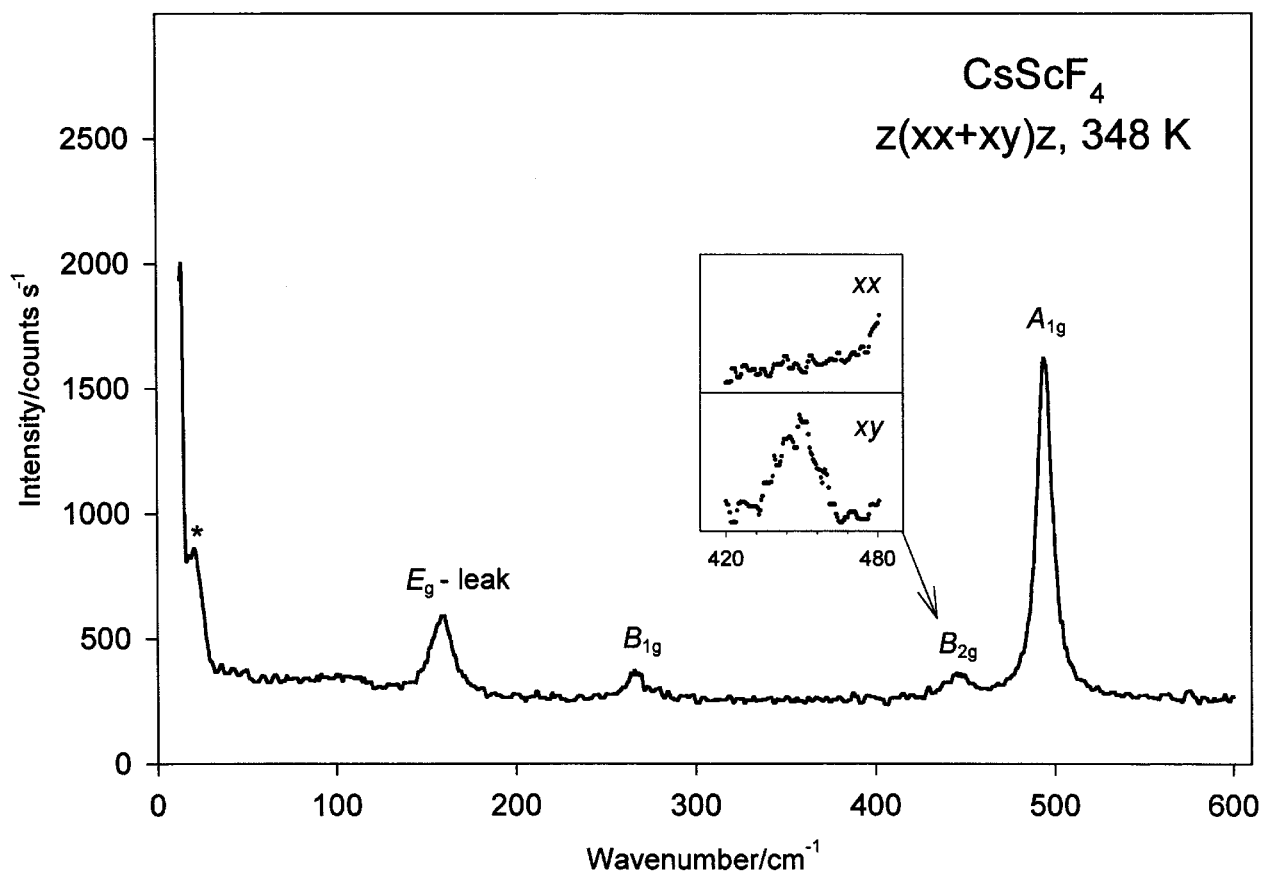
Figure 2. Overview of CsScF$_4$ Raman spectra. $T = 348$ K, $z(xx)z$ and $z(xy)z$ Raman components. Plasma discharge line is marked with an asterisk.
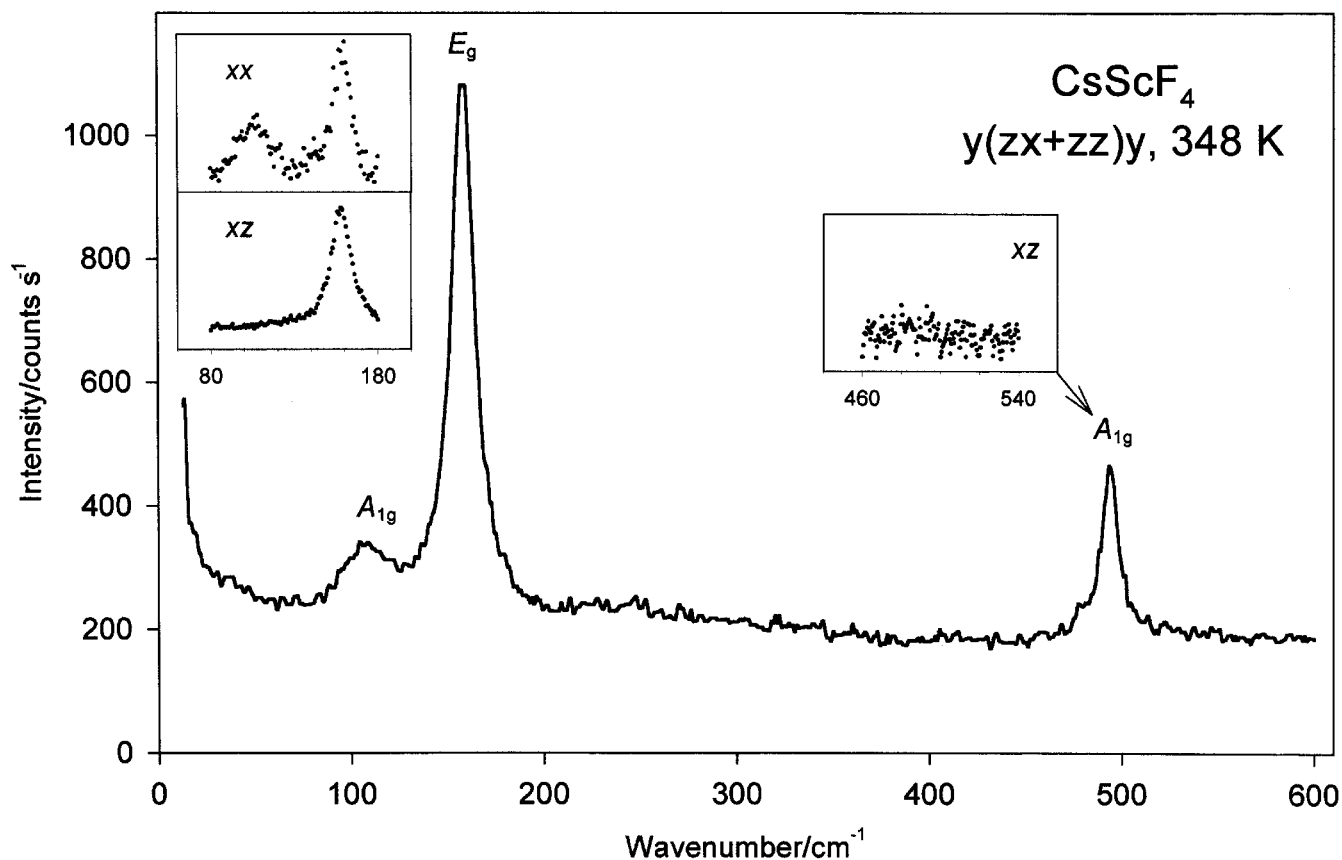
Figure 3. Overview of CsScF$_4$ Raman spectra. $T = 348$ K, $y(zx)y$ and $y(zz)y$ Raman components.
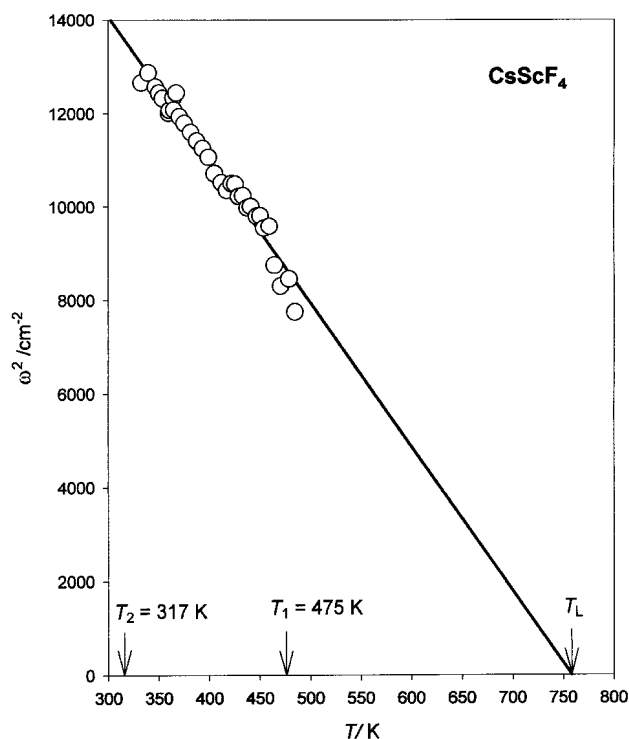
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