Phase transition in the layered perovskite CsScF$_4$ induced by hydrostatic pressure

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Using polarization microscopy and Raman scattering, we have discovered a new phase transition in the layered perovskite crystal CsScF$_4$ under a hydrostatic pressure around 6 GPa. The proposed space group of the high-pressure phase is C_{2h}^2, $Z=4$. © *1999 American Institute of Physics.* [S1063-7834(99)03109-3]

Layered perovskite-like crystals are a traditional models for studying the mechanisms of phase transition; at the same time, numerous practical applications are associated with them (see, e.g., Refs. 1 and 2). The CsScF$_4$ crystal is a typical representative of this family. According to x-ray structural data and measurements of the macroscopic characteristics of this crystal,[3] the structure of its high-temperature phase (space group D_{4h}^1, $Z=1$; see Fig. 1) consists of four layers of linked ScF$_6$ octahedra, separated by Cs$^+$ ions. Upon cooling below 475 K a first-order transition of displacement type occurs, similar to a second-order transition, to the phase D_{4h}^5 with a doubling of the unit cell and, upon further cooling below 317 K, to the rhombic phase D_{2h}^{13}, $Z=4$ (Refs. 3 and 4). This sequence of phase transitions is unusual for cesium-containing perovskites[1,2] and is analogous to that observed in RbAlF$_4$ (Refs. 5 and 6).

In a KAlF$_4$ crystal, which is isomorphic to RbAlF$_4$, a transition to the phase C_{2h}^2, $Z=4$ is also observed at 260 K, and also at room temperature under a hydrostatic pressure around 0.25 GPa;[7] however, efforts to observe an analogous transition in RbAlF$_4$, and over a wide temperature interval in CsScF$_4$ (Refs. 3 and 4), have not yielded positive results. It was in response to this situation that the present study of the effect of high hydrostatic pressures on CsScF$_4$ was undertaken.

Samples of CsScF$_4$ were investigated under conditions of high (up to 10 GPa) hydrostatic pressure on a setup with diamond anvils similar to the one used in Refs. 7 and 8, at room temperature. We investigated samples of the same crystallization as in Refs. 1 and 4; the diameter of the chamber with the sample was 0.25 mm, and its height—0.1 mm. In light of the pronounced layered structure of the crystal, the samples were oriented in the chamber so that observation takes place along the four-fold axis of the tetragonal phases of the crystal (the Z axis in Fig. 1). The pressure was determined with an accuracy of 0.05 GPa from the shift of the luminescence band of a ruby microcrystal[8,9] placed alongside the sample. As the pressure-transmitting medium we used a mixture of ethyl and methyl alcohols or glycerin. Raman

scattering spectra were excited by radiation from an Ar$^+$ laser (514 nm, 0.5 W) and recorded on an OMARS 89 (Dilor) multichannel spectrometer. In light of the small dimensions of the sample and the strong diffuse scattering from its domain structure, we recorded the high-frequency (300–600 cm^{-1}) part of the spectrum, where the valence vibrations of the Sc–F bound of the axial fluorine atoms (F3–Sc–F4 in Fig. 1). From the characteristic low-frequency shift of the analogous vibration line of Al–F we probed the phase transition in KAlF$_4$ (Ref. 7). Simultaneously, we observed the domain structure of the sample with the help of a polarizing microscope.
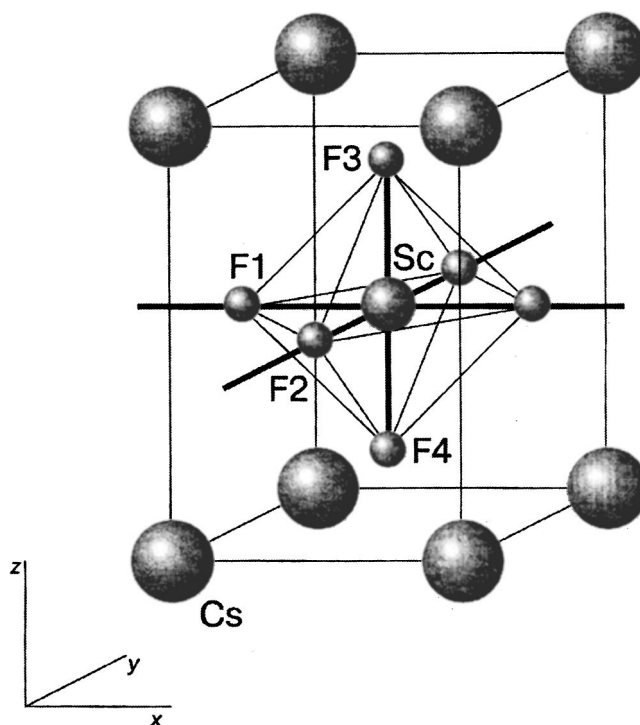

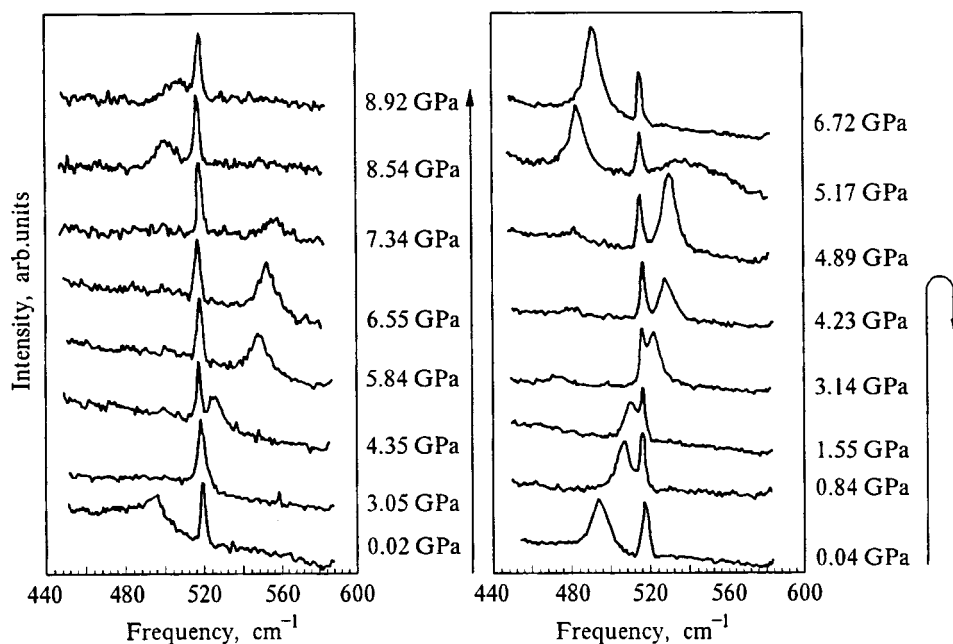FIG. 1. Structure in one unit cell of the high-temperature phase of CsScF$_4$

FIG. 2. Variations of the Raman scattering spectra under pressure. The narrow $520 \, cm^{-1}$ line in the center is the reference line of the gas-discharge. The arrows to the right show the direction of variation of the pressure with which the experimental points were approached.

We carried out two series of measurements: in the one case the pressure was increased monotonically with stops to record the spectra; in the other case, before recording the spectra we lowered the pressure by $0.5–1 \, GPa$ to estimate the magnitude of possible hysteretic effects.

At normal pressure the crystal is found in the rhombic phase D_{2h}^{13}. In the indicated spectral region one intense line is observed at $495 \, cm^{-1}$; a weakly expressed, uncolored system of 90-degree domains is visible in the microscope. As the pressure is increased, the system of domains acquires more contrast (which corresponds to departure from the point of the $D_{4h}^{5} \rightarrow D_{2h}^{13}$ transition) and the frequency of the observed line grows linearly ($7.8 \, cm^{-1}$/GPa).

In the region above $6 \, GPa$ the picture changes abruptly. A new domain structure appears suddenly, as if with a jump: the orientation of the domain walls remains the same as before, but the new structure has a bright interference color, and the domains are larger. With further increase of the pressure, the interference colors change in a continuous fashion. In this case, a dramatic broadening and decrease in the intensity of the observed line take place (Fig. 2); in the series of measurements with continuous increase of the pressure, this happens at $6.6 \, GPa$, the width of the line increases by four- to fivefold up to $40–50 \, cm^{-1}$, while above $8.5 \, GPa$ the line is no longer observed. In the runs with partial lowering of the pressure the corresponding jump takes place at $5.6 \, GPa$, and this line disappears completely at $7.5 \, GPa$. In both cases, the position of the maximum of this wide line changes very little with pressure: $1.8 \, cm^{-1}$ GPa. At the same time, a new intense line at a lower frequency, $490 \, cm^{-1}$, appears in the spectrum immediately after the transition and with further increase of the pressure shifts linearly upward ($7.5 \, cm^{-1}$/GPa).

The observed transition has a pronounced hysteresis of $1–1.5 \, GPa$, which is clearly visible in Fig. 2, and is reversible. The appearance of interference coloring of the domains and its continuous variation are indications of low symmetry

(not higher than monoclinic) of the newly formed phase, which allows variation of the orientation of the optical indicatrix. The shift of the frequency of the Sc–F valence vibration toward lower frequencies correlates with the presumed structure of the phase, C_{2h}^{2}, in which a shift of perovskite-like layers leads to an increase in the distances between fluorine atoms of neighboring layers and a decrease in the corresponding force constant (Fig. 3). An analogous low-frequency shift was observed during the transition to this phase in the spectrum of $KAlF_4$ (Ref. 7). Such a strong dis-
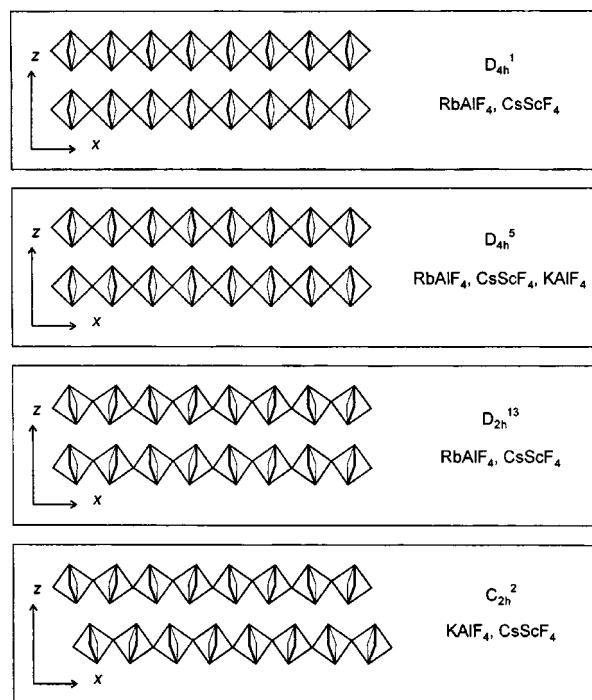

FIG. 3. Packing diagram of the ScF_6 octahedra in different phases of $CsScF_4$ and isomorphic crystals.

tortion of the structure during the transition should lead to formation of pronounced domain walls and a large number of defects, which can explain the pulling of the high-frequency line above the transition point.

To sum up, the above study has made it possible for the first time to observe the transition to the new low-symmetry phase of $CsScF_4$ induced by hydrostatic pressure around 6 GPa. The first-order transition is accompanied by a hysteresis of 1–1.5 GPa. All the observed experimental facts agree with the assertion that the observed phase is isomorphic to the high-pressure phase of $KAlF_4$ with space group C_{2h}^2, $Z = 4$.

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