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# First-principles studies of phonon softening in rocksalt AgF under pressure

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## Abstract

*Ab initio* calculations within the framework of density-functional perturbation theory employing the generalized gradient approximation have been performed to study the lattice dynamics and elastic properties for rocksalt (RS) silver monofluoride (AgF) under pressure. The longitudinal and transverse acoustic phonon modes at the zone boundary  $X$  (0.0 0.0 1.0) point were predicted to be completely softened at 4.7 GPa. This softening behavior is suggested to be the physical driving force for the phase transition from the RS structure to the CsCl structure. Moreover, a pressure-induced softening of the shear modulus in  $C_{44}$  is also verified. However, instead of  $C_{44}$  instability, it is found that the phonon instability dominates the pressure-induced structural phase transition for AgF.

## 1. Introduction

Silver halides are of paramount importance as photographic materials [1], as solid electrolytes [2], and as liquid semiconductors [3]. These compounds can be considered as 'I–VII' compounds, which are ionic counterparts to the group IV and III–V semiconductors. However, their bonding character is not purely ionic and the I–VII compounds span the boundary between predominantly covalent systems characterized by fourfold coordinated structure and ionic ones possessing a sixfold coordinated arrangement. At ambient temperature and pressure, AgI exists as two-phase mixtures of the tetrahedrally coordinated cubic zincblende (ZB) structure and its hexagonal wurtzite (WZ) counterpart, while AgF, AgCl and AgBr adopt the octahedrally coordinated rocksalt (RS) structure that is characteristic of ionic bonding [4].

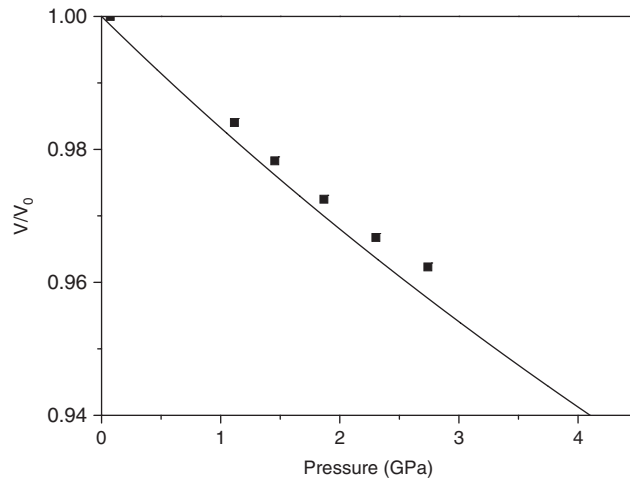
Hydrostatic pressure favors transitions to more densely packed structures and the increasing coordination numbers is, therefore, associated with changes in the bonding character. The structural behaviors of the three silver halides under compression have been studied

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extensively using both experimental and theoretical approaches [5–10]. The structural characterization of the phase transitions in AgCl, AgBr, and AgI were previously investigated using angle-dispersive x-ray diffraction with an image-plated device [5, 7]. In AgCl, the ambient-pressure RS phase transforms to a monoclinic structure at  $p = 6.6$  GPa and then to an orthorhombic TII-type configuration at  $p = 10.8$  GPa. Both AgBr and AgI undergo RS  $\rightarrow$  KOH-type structural transitions at  $p = 7.9$  and 11.3 GPa, respectively. However, as the most ionic compound of the silver halides, the structural behavior of AgF is different from that of the other silver halides (AgCl, AgBr, AgI). The RS AgF was found to undergo a phase transition around 2.8 GPa [8] and it was suggested to be a transformation to the CsCl structure, which is the first high-pressure phase of alkali halides [9]. Interestingly, the reverse CsCl  $\rightarrow$  RS transformation on decreasing pressure occurs via an intermediate phase which possesses an anti-NiAs configuration [10]. On the theoretical side, Gupta *et al* [11] employed a three-body-potential approach to describe the phase transitions and equation of states (EOS) for AgCl and AgBr. However, they suggested that the RS structure will transform directly to the CsCl structure based on the structural similarities between the alkali halides and the silver halides. Meanwhile, Nunes *et al* [12] presented a first-principles study of the relative stability of a few different structures, namely AgCl, AgBr, and AgI. They suggested that AgCl and AgBr might prefer a rhombohedral phase induced from the RS structure with pressure. As for AgI, the first high-pressure phase is considered to be RS structure, and the subsequent phase has not been determined. In AgF, however, the physically driven mechanism of the pressure-induced structural phase transition from the RS structure to the CsCl structure remains unclear. Dynamic instabilities are often responsible for phase transitions under pressure [13, 14]. Lattice dynamics therefore plays an important role in understanding the mechanisms of phase transitions. In our previous works, the different mechanisms driving the phase transitions in copper halides [15, 16] and silver halides [17] (AgCl and AgBr) are clearly revealed by the accurate *ab initio* determination of the transverse acoustic phonon softening. Consequently, in this work, *ab initio* investigations of lattice dynamics are, thus, carried out to probe the nature of pressure-induced phase transformation in RS AgF.

## 2. Computational details

Phonon frequencies and the projected phonon density of states (DOS) were calculated using a plane-wave pseudopotential scheme [18] within the framework of density-functional theory [19, 20] and linear response theory [21, 22] implemented in the Quantum-ESPRESSO package [23]. The norm-conserving pseudopotentials were generated using the method of Troullier and Martins [24]. The generalized gradient approximation (GGA) of the exchange–correlation functional is used [25]. The convergence tests gave kinetic energy cutoffs of 100 Ryd with a  $14 \times 14 \times 14$  Monkhorst–Pack (MP) grid for the electronic Brillouin zone (BZ) integration. A  $4 \times 4 \times 4$   $q$  mesh in the first BZ is used in the interpolation of the phonon calculations. Elastic constants were obtained from evaluations of the stress tensor generated by small strains using the density-functional plane-wave technique, as implemented in the CASTEP code [26]. The equilibrium lattice constant has been determined by calculating the total energy as a function of volume. Fitting the Murnaghan equation of state [27] to the total energies versus lattice parameters yields the equilibrium lattice parameter  $a_0$ , bulk modulus  $B_0$ , and the pressure derivative of the bulk modulus  $B'_0$ , respectively. The calculated equilibrium lattice parameters and bulk modulus, together with previous full potential linearized augmented plane-wave (FP-LAPW) theoretical calculations [28] and the experimental data [29], are listed in table 1. It is found that the current theoretical lattice constant is in good agreement with experimental data within 3%, thus it strongly supports the choice of pseudopotentials and the



**Figure 1.** Comparison of the calculated equation of state (solid line) for AgF with the experimental data (solid square) from [10].

**Table 1.** Calculated equilibrium lattice parameter ( $a$ ), bulk modulus ( $B_0$ ), and the pressure derivative of bulk modulus ( $B'_0$ ) for AgF. Previous theoretical calculations from [28] and experimental results from [29] and [10] are also shown for comparison. The units for  $a$  and  $B_0$  are in Å and GPa, respectively.

	$a$	$B_0$ (GPa)	$B'_0$
Reference [28]	5.036	63.3	2.74
Experiment	4.936 <sup>a</sup>	61(2) <sup>b</sup>	—
This work	5.074	56.8	4.89

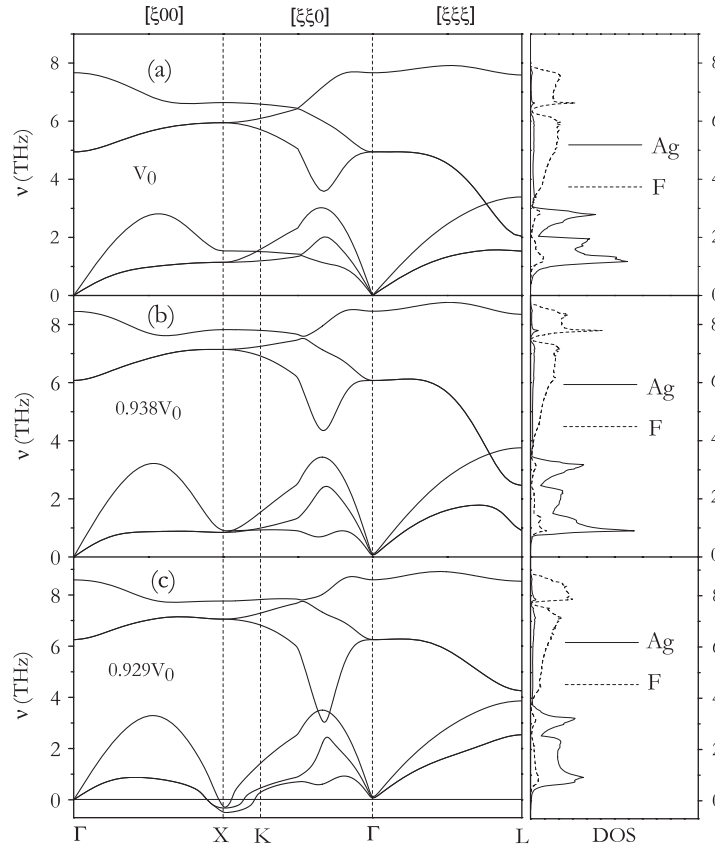
<sup>a</sup> Reference [29].

<sup>b</sup> Reference [10].

GGA approximation for the current study. It is noteworthy that the theoretical lattice constant is larger than that of the experimental results. This is the typical deviation of GGA calculation. The calculated EOS of AgF in RS structure is compared with the experimental data [10] as shown in figure 1. It is clear that the theoretical calculation correctly predicts the trend of the observed variation of volume with pressure. Therefore, the overall good agreement between theory and experiment in EOS encourages us to explore further the high-pressure properties of this material.

### 3. Results

The phonon dispersion curves along high-symmetry lines and the projected phonon DOS for AgF at different volumes are shown in figure 2. There is no experimental data available on the whole phonon dispersion curves for bulk RS AgF in the literature. Thus, the present work provides the phonon dispersion curves at ambient pressure for the first time, as shown in figure 2(a). The features of the phonon spectrum for AgF are similar to those for AgCl and AgBr [17], such as the shoulder in the longitudinal optical (LO) ( $[\xi\xi0]$ ) branch near the  $\mathbf{K}$  point, the low-lying transverse optical (TO) branch along the direction of  $[\xi\xi\xi]$ , and the minimum in the LO branch along the direction of  $[\xi00]$ . Since the Ag atomic mass is heavier than that of the F atom, the Ag atomic vibrations dominate the low phonon frequencies in the projected phonon DOS, as plotted in the right-hand panel of figure 2(a).



**Figure 2.** Calculated phonon frequencies and projected DOS of AgF at different volumes.

The far-infrared absorption spectrum of AgF has been measured at 143 K in the region of the lattice vibrations [29]. The frequencies of TO ( $\Gamma$ ) and LO ( $\Gamma$ ) modes were determined by the one-phonon absorption process. In addition, there were two other minima in the transmission spectra, and they probably arise from two-phonon absorption processes. Symmetry considerations identify these minima as the summation bands TO + TA and TO + LA at the point  $L$  of the BZ edge. Table 2 shows the calculated frequencies of the phonon modes TO ( $\Gamma$ ), LO ( $\Gamma$ ), TO + TA ( $L$ ) and TO + LA ( $L$ ), together with the experimental results [29]. The agreement between the theory and experiment in the frequencies of TO( $\Gamma$ ), LO ( $\Gamma$ ) and TO + LA ( $L$ ) are satisfactory. Meanwhile, the calculated frequency of the TO + TA ( $L$ ) mode is  $119 \text{ cm}^{-1}$ , which is underestimated by up to about 46% relative to the experimental result. There are two possible reasons for the large deviation. First, since it is difficult to prepare pure bulk solid of AgF suitable for spectroscopic examination, the far-infrared transmission was measured on the film of AgF. Therefore, this large discrepancy may be attributed to the difference in the characteristics of the bulk and film of AgF, respectively. Second, the two-phonon processes may not arise from the summation bands of TO + TA ( $L$ ) and TO + LA ( $L$ ) but from the other modes. In the RS structure, there is a total of four different kinds of infrared-active two-phonon combinations at the  $L$  point, which are TO + LA, TO + TA, LO + LA, and LO + TA [30]. We note that our calculated frequencies of the TO + LA ( $L$ ) and LO + TA ( $L$ ) modes are  $181$  and  $303 \text{ cm}^{-1}$ , respectively. These two frequencies might

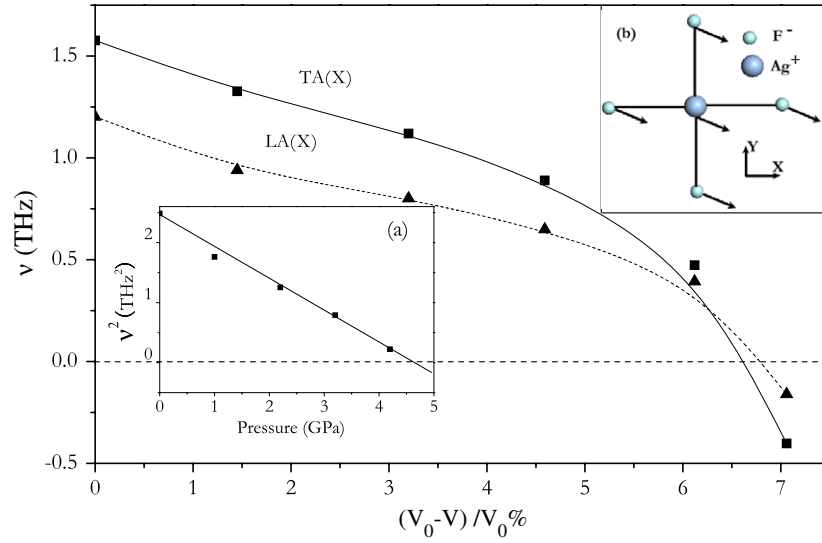
**Table 2.** Theoretical phonon frequencies of different modes and the experimental results at 143 K from [29]; the unit is  $\text{cm}^{-1}$ .

	TO ( $\Gamma$ )	LO ( $\Gamma$ )	TO + TA ( $L$ )	TO + LA ( $L$ )
This work	165	256	119	181
Reference [29]	176	322	221	273

account for the two additional minima at 221 and 273  $\text{cm}^{-1}$  in the transmission spectra [29]. In this case, the deviation of the frequencies between theory and experiment is only up to about 14%. Therefore the two-phonon processes reflected from the additional two minima may arise from the summation bands TO + LA( $L$ ) and LO + TA( $L$ ) instead of TO + TA ( $L$ ) and TO + LA ( $L$ ). The discrepancy between theory and experiment may result from the neglect of temperature effects, which might be significant.

In figures 2(b) and (c), one observes that, with decreasing volume, all the optical phonon modes shift to higher frequencies, while the acoustic phonon modes at the zone boundary  $X$  (0.0 0.0 1.0) point decrease in frequency, indicating negative mode Grüneisen parameters,  $\gamma_j(q) = -\partial \ln \nu_j(q) / \partial \ln V$  for mode  $j$ , where  $q$  is the wavevector,  $\nu$  is the frequency, and  $V$  is the volume. At a volume of  $0.929V_0$  (where  $V_0$  is the theoretical equilibrium volume), the frequencies of the longitude (LA) and transverse acoustic (TA) phonon at the  $X$  point decrease to be imaginary, signaling a structural instability in the RS phase. It is very interesting to note that the LA phonon mode at the  $X$  point in AgF also decreases with pressure. This behavior is in apparent contrast to those of AgCl and AgBr, in which the LA( $X$ ) phonon frequency increases with pressure [17].

The variations in the frequencies of the TA( $X$ ) and LA( $X$ ) modes with pressure are shown in figure 3. From the main figure, it is clear that the volumes at which the frequencies of TA( $X$ ) and LA( $X$ ) soften to zero are  $0.934V_0$  and  $0.932V_0$ , respectively. The frequencies of the two phonon modes almost soften to zero at the same volume within numerical error. This indicates that both TA and LA phonon instabilities might contribute to the structural phase transition of AgF. The RS AgF would become unstable at a critical pressure  $P_c$  at which the frequency of the TA( $X$ ) mode becomes zero. In an attempt to estimate  $P_c$ , the pressure dependence of the TA( $X$ ) mode frequency was fitted by a phenomenological function [31] of  $\nu^2 = (\nu_0^2 - aP)$ , as shown in the inset (a) of figure 3. As a result,  $P'_c$  giving  $\nu = 0$  is estimated to be 4.7 GPa ( $0.934V_0$ ) for RS AgF. Since the transition between RS and CsCl is of first order, the phase transition is suggested to occur below  $P_c$ , as  $P_c$  is the upper limit [32]. Therefore, the difference between the transition pressure of  $\sim 4.7$  GPa predicted by phonon instability and  $\sim 2.7$  GPa by experiment is acceptable. The other origin of this difference may be attributed to the neglect of temperature effects. The schematic representation of eigenvectors for the TA soft phonon mode at the  $X$  point is shown in the top view of the (001) plane of the RS structure in the inset (b) of figure 3. The eigenvectors of the Ag cation and F anion are antiparallel in the primitive cell while they are parallel in the (001) plane, and the atomic displacement forms an angle of  $38.9^\circ$  with respect to the direction [100]. Phonon softening usually corresponds to the instability of a particular atomic movement. The RS AgF, therefore, tends to become unstable with respect to the atomic displacement corresponding to the soft mode. Therefore, it can be concluded that the atomic movements along the directions of the eigenvectors in the (001) planes is closely related to the phase transition from the RS structure to the CsCl structure. Generally, one can search for the new structure from the soft mode by distorting the atoms along the directions of eigenvectors and, then, fully optimizing the structure. In many cases [13, 33], this procedure will generate the lowest-energy structure. In this study, we search for the local

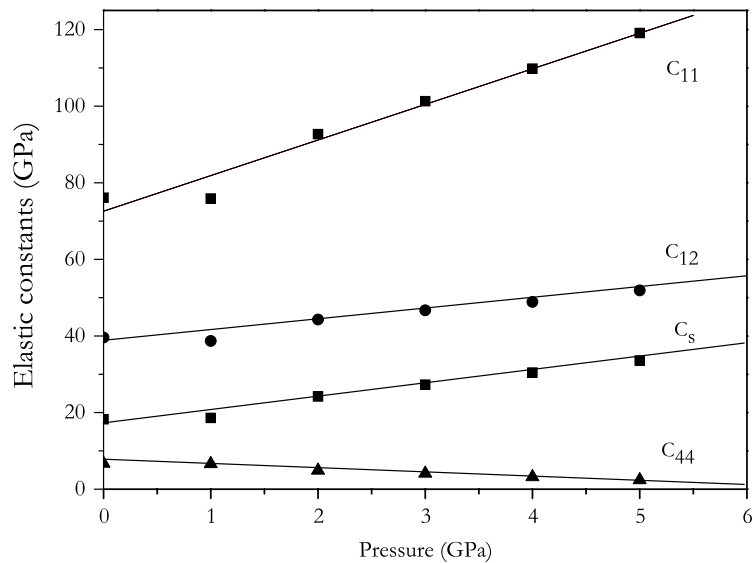


**Figure 3.** Main figure: calculated TA (solid line and square symbols) and LA (dashed line and triangle symbols) phonon frequencies at the  $X$  (0.0 0.0 1.0) point of the BZ in AgF as a function of volume. The solid line through the calculated data points represents fitted curves using a B-spline. Inset: (a) the calculated squared phonon frequency  $\nu^2$  as a function of pressure—the solid line through the data points is a linear fit; (b) the eigenvector for the TA soft phonon mode at the  $X$  point. The Ag atom is located at (0 0 0). The other four F atoms sit at (1/2 0 0), (−1/2 0 0), (0 1/2 0), and (0 −1/2 0), respectively. The eigenvectors of the Ag cation and F anion are parallel in the (001) plane, and the eigenvectors form an angle  $38.9^\circ$  with respect to the [100] direction. The arrows show the directions of atomic displacements.

(This figure is in colour only in the electronic version)

energy minimum by displacing atoms along the eigenvectors of the TA( $X$ ) mode and relaxing the resulting structure. But the expected CsCl structure with the lowest energy cannot be found using the above procedure. The reason might be that the energy gain is determined not only by the curvature of the energy surface but by higher-order terms as well as the strength of coupling to the strain and other modes, both unstable and stable [34, 35]. Since the pressures at which the TA ( $X$ ) and LA( $X$ ) modes become unstable are very close, the softening mode TA( $X$ ) may drive the phase transition for AgF by coupling with the mode LA( $X$ ). Therefore, the global energy minimum cannot be found correctly just by moving the atoms along the directions of the eigenvectors corresponding to the softening mode TA( $X$ ).

The variations in the elastic constants with pressure for RS AgF are shown in figure 4. One observes that  $C_{11}$ ,  $C_{12}$  and  $C_s = 1/2(C_{11} - C_{12})$  show linearly increasing trends with pressure, while  $C_{44}$  shows a linear softening trend. It is noteworthy that, although  $C_{44}$  softens with pressure, it still remains positive under pressure, at which the phonon softens to zero frequency for AgF (4.7 GPa). This  $C_{44}$  softening behavior is quite similar to those in AgBr and AgCl [17]. It should also be pointed out that the phonon instabilities occur at the points away from the center of the Brillouin zone and appear before the material becomes elastically unstable, according to the elastic stability criteria  $C_{44} > 0$  and  $C_s > 0$ . Therefore, it is concluded that the pressure-induced structural phase transition for AgF is not induced by the  $C_{44}$  instabilities, which is related to the long-wavelength part of the transverse branch near the center of the first BZ. But the softening behavior of the shear modulus  $C_{44}$  might have an indirect relation to the transition from the RS phase to the CsCl phase for AgF.



**Figure 4.** Calculated elastic constants (solid symbols) of  $C_{11}$ ,  $C_{12}$ ,  $C_s$ , and  $C_{44}$  for AgF with pressure in the RS structure. The solid lines are the linear fits to the calculated results.

#### 4. Conclusion

In conclusion, the phonon dispersion curves for AgF are calculated at different volumes using density-functional linear-response theory. Both the TA and LA phonon modes at the  $X(0.0\ 0.0\ 1.0)$  point were found to decrease with pressure. These phonon softening behaviors contribute to the phase transition from the RS phase to the CsCl phase. Further analysis performed on the elastic constants under pressure suggested that the shear instabilities in  $C_{44}$  may have an indirect relation to the structural phase transition for RS AgF.

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