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New Ideas about Old Chestnuts: PhaseTransitions in Perovskites

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The formula of perovskites can be expressed as ABX_3, A and B representing cations, and X an anion. The aristotype structure consists of an array of perfectly regular and un-tilted BX_6 octahedra that share corners to form a three-dimensional framework within the cavities of which lie the A cations in twelve-fold coordination by the X anions. Perovskites with lower symmetries at ambient conditions generally exhibit a series of phase transitions with increasing temperature to higher symmetry structures with smaller tilts, the end-point being the cubic structure with no tilts and Pm3m symmetry. These high-temperature transitions are traditionally considered as involving changes in the pattern of tilts of effectively rigid octahedra in which octahedral distortions play an insignificant role. If the octahedra were truly rigid, then the connectivity of the structure means that a decrease in the magnitude of the tilts of the octahedra, whether continuously within a phase or at a phase transition, must be accompanied by an increase in the unit-cell volume. Therefore, the only way in which the volume of such a structure can be reduced is through an increase in the tilts of the octahedra. Pressure must therefore result in either an increase in tilting of the rigid octahedra without a change of symmetry, or a phase transition to a structure of lower symmetry, greater tilts and smaller volume. Pressure is therefore predicted to have the same effect on these structures as decreasing temperature, and the phase transition boundaries will therefore have slopes dTc/dP > 0. Recent experiments have now shown that many perovskites instead undergo transitions to higher-symmetry, less tilted structures with increasing pressure and exhibit phase transition boundaries with dTc/dP < 0. This behaviour is a direct consequence of the compressibility of the BX_6 octahedra, which is thus shown to play an essential role in determining the phase transition behaviour of perovskites [1].

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Ab Initio Simulations of Pressure-Driven Phase Transitions of Silver Halides

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Silver halides show a complex polymorphism on increasing pressure, with transitions relating phases where the coordination number of cations and anions may range from 4 to 6, 7 and 8. Experimental results are available from X-ray and neutron diffraction studies [1,2], but the whole desirable pressure range is not covered. Further, some intermediate phases with limited pressure stability ranges are observed, which are interesting because they may represent metastable structural intermediates in similar transformations of other compounds. For these reasons, theoretical investigations of these systems by quantum-mechanical methods are particularly attractive. We have already studied some features of the low-pressure range transitions of AgI (zincblende-to-antilitharge-to rocksalt) [3], and of those of AgCl [4], with emphasis on the interpretation of the kinetic mechanisms. Here results are reported concerning the thermodynamic aspects of phase transformations of AgI and AgCl in the high-pressure range, where the phase sequence is rocksalt- ($Fm\bar{3}m$) to KOH- ($P2_1/m$) to TlI- ($Cmcm$) to CsCl-type ($Pm\bar{3}m$) structure. *Ab initio* periodic calculations of the ground-state total energy E were performed by the CRYSTAL code [5], based on localized basis functions (Gaussian-type atomic orbitals), and employing B3LYP and DFT-GGA Hamiltonians. The structural parameters were optimized at selected values of constant pressure p, by the enthalpy ($H=E+pV$) minimization principle. Both transition I ($Fm\bar{3}m$ to $P2_1/m$) and II ($P2_1/m$ to $Cmcm$) have a displacive-ferroelastic character, which can be represented by the $\eta = -(2c\cos\beta/a)$ order parameter. Enthalpy profiles $H(\eta)$ were computed for the whole η range from 0 ($Fm\bar{3}m$) to 1 ($Cmcm$) at different p values, with full optimization of the monoclinic $P2_1/m$ structure. Transition II is shown to be of second-order type, whereas transition I has a significant activation enthalpy (0.010 eV at the computed equilibrium pressure of 19.3 GPa), and is thus first-order. This is confirmed by the simulated behaviour of lattice constants vs. pressure. The structural evolution throughout the transformation path was also fully characterized.

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