

MS26-O2 Incommensurate oxides and sulfidesBerthold Stöger¹

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The defining property of a crystal has for a long time been its three-dimensional periodicity. With the advent of X-ray diffraction, a seemingly equivalent property of crystals emerged, namely their discrete diffraction pattern. But already in 1927 Dehlinger [1] observed sharp "lattice ghosts" in cold-formed metals, which are incompatible with lattice periodicity. These additional reflections emerge from structural modulations of a basic structure with an incommensurate periodicity.

The superspace approach [2] provides the necessary theoretical foundation to conveniently describe such incommensurately modulated phases and their diffraction patterns. It resulted in an explosion of the number of known incommensurates [3] and the realization that quasiperiodicity is distinctly less rare than one might expect. Nevertheless, the existence of incommensurates still appears mysterious and counterintuitive.

To demonstrate the ubiquity and variety of these phases, several incommensurate oxides and sulfides are presented. The thortveitite family is made up of transition metal diphosphates, diarsenates or divanadates with the general formula $M_2X_2O_7$ ($X=P, As, V$). The members feature a complex crystal chemistry with commensurately and incommensurately modulated phases. The modulation is a dynamic phenomenon as evidenced by a complex phase transition behavior. Analogous phenomena are observed in the condensed phosphates and arsenates $Tl_3P_3O_{14}H_8$ and $Rb_3AlAs_3O_{12}$ and the orthophosphate $K_3PO_4 \cdot 3H_2O$.

In the ditellurates(IV) MTe_2O_8 ($M=Ca, Sr, Cd$) and their solid solutions, on the other hand, modulation is due to an occupational modulation of the O atoms. Accordingly, these phases do not feature structural phase transitions. Such complex static occupational modulations are likewise observed in natural sartorite and roschinite sulfosalts. Here, the modulation periodicities depend on subtle variations of the composition.

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MS26-O3 Structural phase transitions in the organic-inorganic hybrid perovskitesSébastien Pillet¹, Bendeif El Eulmi¹, Yangui Aymen^{2,3}, Triki Smail¹, Abid Younes³, Boukheddaden Kamel²

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Organic-inorganic hybrid perovskites have recently emerged as highly efficient optoelectronic materials, and are being intensively investigated and developed for high performance photovoltaics, photodetections, light-emitting diodes and laser devices. These materials exhibit a structural topology derived from the ABX_3 perovskite structure, consisting of a corner-sharing BX_6 octahedral network completed by organic A cations. Depending on the size of the organic cation, 3D, 2D, and 1D systems have been reported.

The compounds $(C_6H_{11}NH_3)_2[PbX_4]$ ($X=I, Br, Cl$) exhibit a 2D structural architecture with semi-conducting inorganic layers of corner-sharing PbX_6 octahedra separated by bilayers of $C_6H_{11}NH_3^+$ cations. The optical properties (absorption and photoluminescence) have been investigated as a function of temperature, and show very interesting and unusual behaviors, such as white light emission, which are connected to structural phase transitions [1-3]. Single crystals of the three compounds and of the solid solutions $(C_6H_{11}NH_3)_x[PbI_{4-x}Br_x]$ have been investigated through x-ray diffraction as a function of temperature. The corresponding structural phase diagram is very rich, displaying a different sequence of commensurate-incommensurate phase transitions for the bromine and iodine derivatives, characterized by a distortion and modulation of the inorganic perovskite layer. The mixed-halide series $(C_6H_{11}NH_3)_2[PbI_xBr_{4-x}]$ obtained by gradual substitution of Br by I exhibits a morphotropic structural transition, which allows tuning the optical properties.

The complete structural phase diagrams and phase transitions will be described and discussed in connection to the temperature dependence of optical properties.

References

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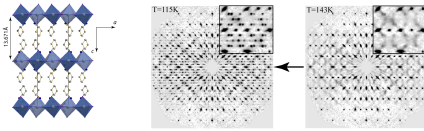


Figure 1. (left) crystal structure of $(\text{C}_6\text{H}_{11}\text{NH}_3)_2[\text{PbI}_4]$. (right) commensurate-incommensurate structural phase transition.

Keywords: hybrid perovskite, phase transition, incommensurate structure

MS26-O4 Probing the nuclear and magnetic structure of a complex ferromagnetic semiconductor

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The large diversity of structural, electronic, and magnetic phases offered by compounds made up of two or more interpenetrating sublattices (composite structure) such as misfit layer chalcogenides offer the possibility to tune materials functionality using crystal chemistry concepts [1]. The structural and physical properties of the columnar composite crystal $\text{A}_p\text{Cr}_2\text{X}_6$ ($\text{A} = \text{Ba}, \text{Sr}, \text{Eu}, \text{Pb}$; $\text{X} = \text{S}, \text{Se}$; $p \approx 0.29$) have not been studied in details.[2] The difficulty in interpreting the observed physical properties and the uncertainty about the exact chemical composition led to the reinvestigation of the crystal structure by Brouwer and Jellinek [2]. They concluded that the crystal structure of this family of materials could be described as an intergrowth of three structural units which have a common hexagonal basal plane, but different c axes. A three-dimensional network (B_3X_{36}) of triply twined strips of CrX_6 octahedra with a lattice constant of c_0 creates hexagonal funnels containing $\text{A}_6\text{B}_2\text{X}_6$ chains with a lattice parameter c_6 and the triangular tunnels A_3X chains with a lattice parameter c_3 . Here we solve the crystal structure of the $\text{Ba}_{0.712}\text{Cr}_2\text{Se}_{3.712}$ in the superspace group $\text{P6/m}(00\gamma_1)s0(00\gamma_2)00$ (175.2.81.3 in the tables of Stokes and Campbell) using neutron powder diffraction, showing it is not a commensurate supercell but incommensurately modulated and study the evolution of the structural parameters on cooling through the magnetic transition observed at 110 K. This material is a ferromagnetic semiconductor at low temperature, with a measured Seebeck coefficients as large as 100 $\mu\text{V}/\text{K}$ at room temperature. It is thus likely to have low thermal conductivity on account of its complex structure and is thus of interest for thermoelectric applications.

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