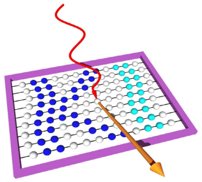

Phase-Instability and Cu-Se-Binding in KCu_2Se_2

HL 12.68

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Theory

- New Layered Materials (prepared in the Bensch group)
- Unconventional Binding
- Phase-Instability
- Full Potential (AFC-ELAPW-kp)

Method

Density of states (DOS) resolved with respect to atomic species and orbital character, band structure and DOS contribution to the total energy have been numerically determined for both the tetragonal and orthorhombic phase.

The calculations have been performed with the augmented Fourier components (AFC) version of an extended full potential linearized augmented plane wave (ELAPW) method.[1,2] The density is separated into two parts: a Fourier part, which represents the charge density of the valence electrons and a narrow MT part, describing the nucleus and the core electron distribution in a spherically symmetric average. The Fourier charge density distribution is easily accessible in this method because the extended LAPW method easily yields the Fourier transform of the valence wave functions.

Technics

All the results presented here were calculated using this AFC ELAPW-kp method. The calculation of all observables is based on self-consistent potentials determined by the AFC method. The basis size of the calculations is about 700 functions for both phases, or about 150 APWs per atom. The parameter $G_{max} \cdot S_{min}$ was around 8.0, where S_{min} is the smallest sphere radius. For the self-consistent calculations, the densities were computed in about 250 k-points. The Fourier decomposition of the wavefunctions needed between 3000 and 5000 plane waves for the tetragonal and orthorhombic phase, respectively. The extension of the basis orbitals had to be enlarged to involve in total 4 additional orbitals per atom and angular momentum for the semicore states of Cu.

[1] E.E. Krasovskii, F. Starrost and W. Schattke, Phys. Rev. B **59**, 10504 (1999)
[2] F. Starrost, E. E. Krasovskii, W. Schattke, J. Jockel, U. Simon, R. Adelung and L. Kipp, Phys. Rev. B (1999) submitted
[3] O. Tiedje, S. Brodersen, F. Starrost, E.E. Krasovskii, C. Ramírez and W. Schattke, Verhandl. DPG VI **34**, 786 (1999)

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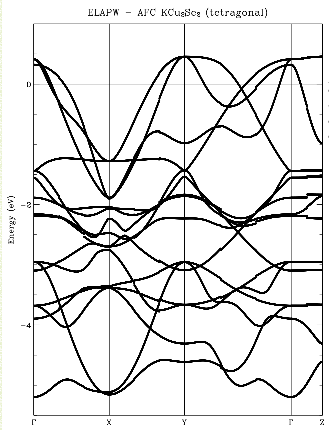
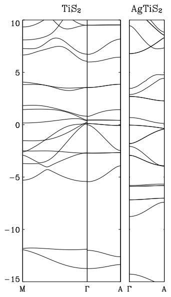
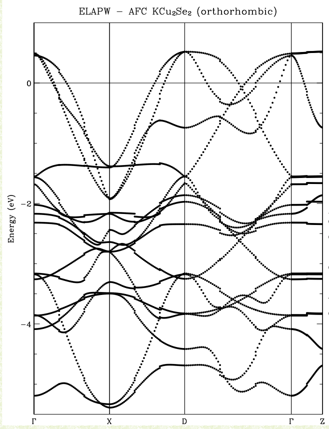
Bandstructure



Tetragonal Phase
- missing dispersion in ΓZ → 2dim. structure
- Cu-d Se-p bands
- metal

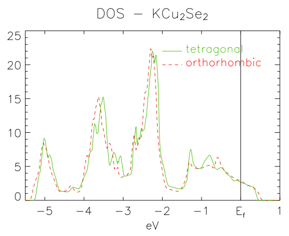


Comparison with (intercalated) Transition-Metal Dichalcogenides [3]
- similar 2dim. electronic structure
- but significant higher conductivity in KCu_2Se_2, even in z-direction



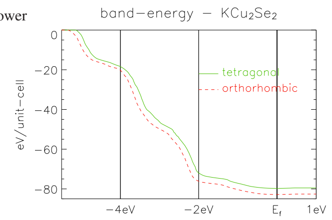
Orthorhombic Phase
- similar bandstructure
- Se-Se-distance increased (2%)
- Se-Cu-distance decreased (2%)
→ stronger dispersion
- shifted downwards for lower energies, upwards for higher energies

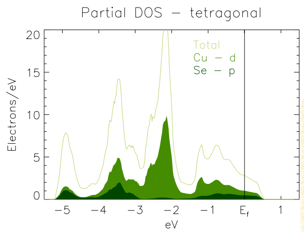
Density of States



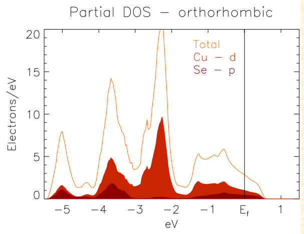
Density of States
- comparision tetragonal - orthorhombic
- earlier onset, shift in orthorhombic phase
- similar at E_f

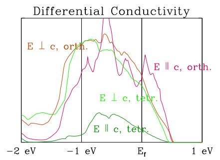
Sum of Kohn-Sham-Energies
- not total energy
- orthorhombic 3eV lower
- see onset of DOS

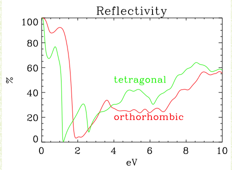




Cu-d and Se-p projected DOS
- hybridization
- electron counting: $2xSe^{1.5-}$,$2xCu^{1+}$,$1xK^{1+}$





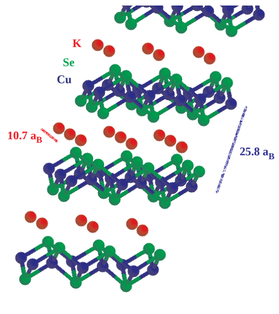


Results

From the electronic structure point of view the discussed compounds show similarities to the well known hexagonal dichalcogenides. Different from the latter and especially interesting appears the theoretically found metallic character related to the presence of Cu as central atom whose d-bands take part in the valence binding and experience a hybridization with the Se-p bands significantly stronger than it is observed e.g. for the Ti central atom in the above hexagonal class of layered crystals. Furthermore, the inter-sandwich K appearing here is reminiscent of alkali intercalation in the latter. The study of both material classes may provide insight into the binding of the so-called misfit structures consisting of interchanging tetragonal and hexagonal sandwiches.

Another interesting property is the value of the Se valency which gives rise to puzzling questions in view of a desired general behaviour and explanation of the binding character.

Geometry



KCu_2Se_2
- layered crystal structure
- tetragonal or orthorhombic
- 5 atoms in the unit-cell
- similarity to hexagonal dichalcogenides