Chemical Bonding in $CuAl_2$ and Isostructural Compounds

Marc Armbrüster, Miroslav Kohout, Frank R. Wagner, Walter Schnelle, Alexander Yaresko, Ulrich Schwarz and Yuri Grin

Introduction

With the tetragonal antiprism as coordination polyhedron of a transition metal atom, $CuAl_2$ shows one of the most simple and very common structural motives for intermetallic compounds. In this project we focus on the bonding situation in the compounds $TiSb_2$, VSb_2, $MnSn_2$, $CoSn_2$, $FeSn_2$ and $CuAl_2$ which all crystallize in the $CuAl_2$ structure type. In order to get a complete picture of the bonding situation from an experimental and theoretical point of view the investigation combined synthesis, measurements of physical properties and quantum chemical calculations.

Description of the crystal structure

The ***I***-centered unit cell of $CuAl_2$, with the symmetry of the space group ***I***4/***mcm***, contains four formula units ***AB***$_2$. The ***A*** atoms (transition metal) are placed on the Wyckoff site 4***a*** (0, 0, 1/4) and the ***B*** atoms (main group element) are situated at position 8***h*** (***x, x***+1/2, 0) with ***x*** = 0.1583. There are at least three different possibilities to describe the crystal structure. (Fig. 1).

Emphasizing the ***A-B*** interaction, columns of base-condensed, tetragonal antiprisms of ***B*** atoms can be recognized along the [001] direction. These columns are sharing half of the side edges forming a three dimensional network. The ***A*** atoms center the antiprisms (Fig. 1a).

Concentrating on the shortest ***B***–***B*** distances ***d***1 and ***d***2 results in a structure where interpenetrating graphite-like nets are formed which extend in the (110) and $(\bar{1}10)$ planes (Fig. 1b).

By connecting all neighboring B atoms (preferred distances ***d***1–***d***4), the structure can be built from three-dimensionally linked ***tetraedersterns*** (Fig. 1c).

In order to find the representation which is in accord with chemical bonding, quantum chemical calculations were performed. A better understanding of the chemical bonding should also help to rationalize the electronic physical properties of these isostructural compounds.

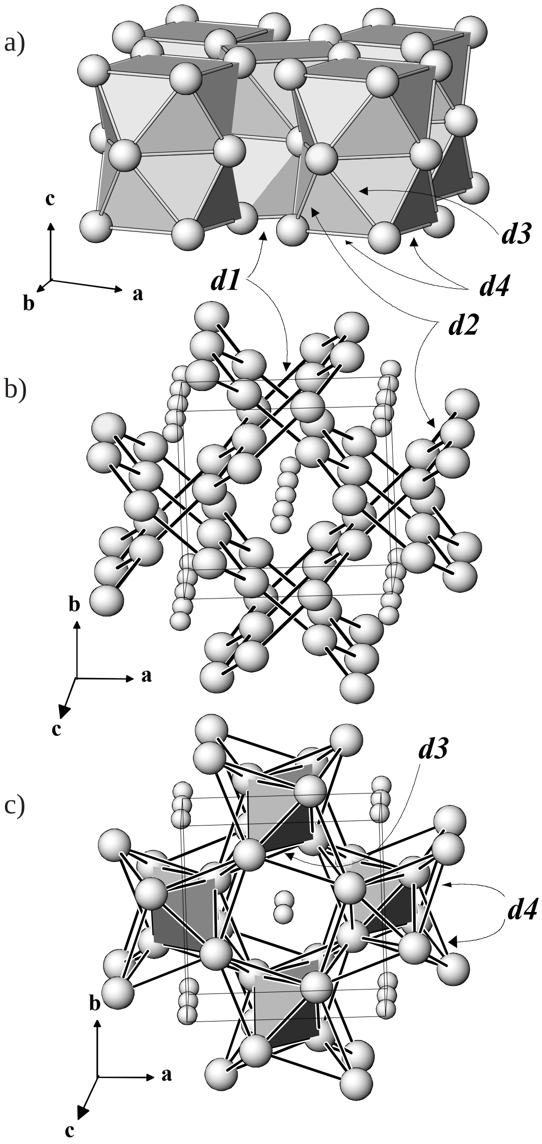

Fig. 1: The different representations of the $CuAl_2$ structure type (small spheres: A atoms; large spheres: B atoms).

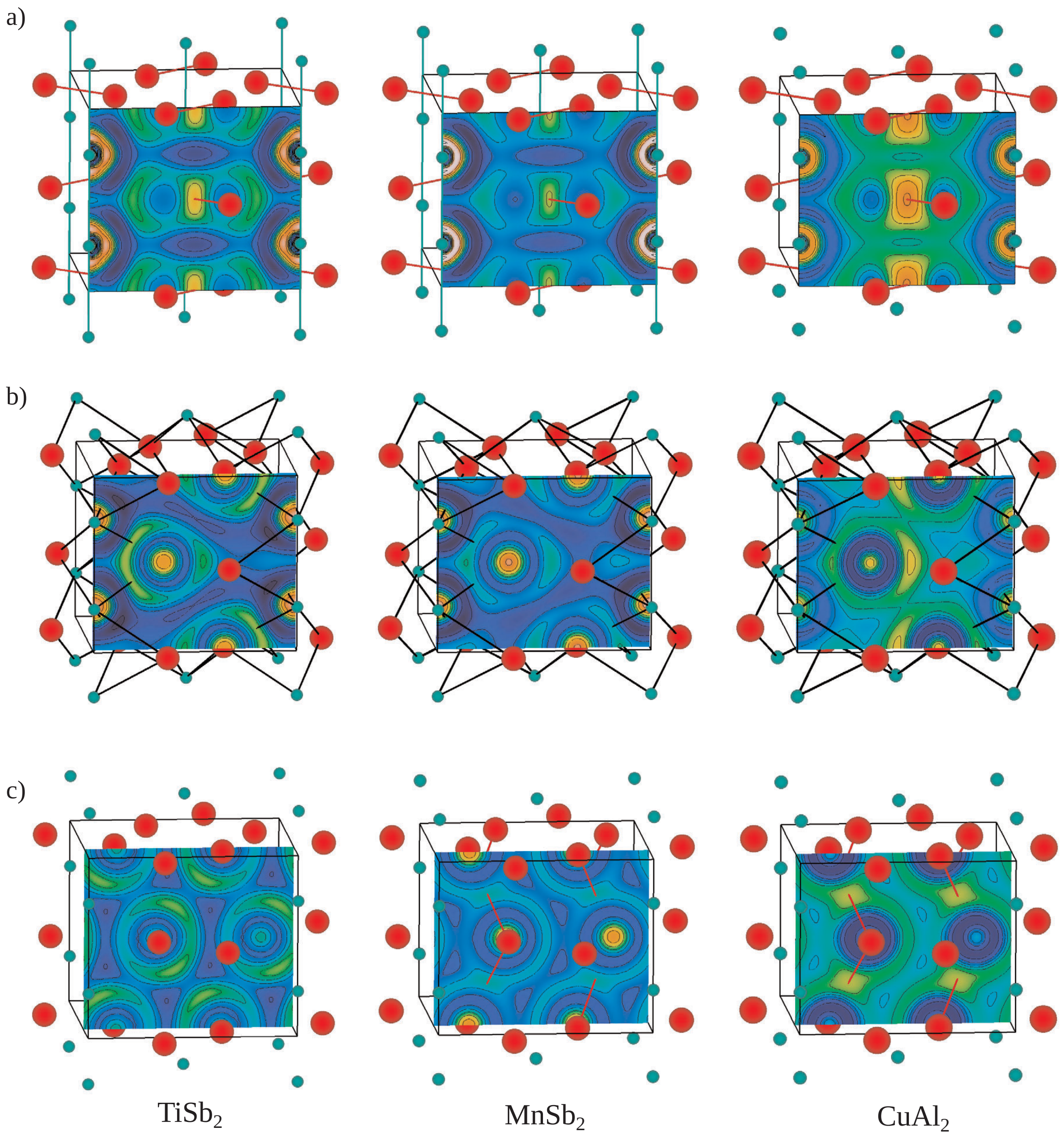

Fig. 2: ELF for representatives of the CuAl$_2$ structure type. The ELF slices are crossing the middle of the distance d1 and include the shortest A-A distance (a), the center of the three-center A-B-A bond (b), and the middle of the distance d2 (c). A maximum in the ELF (yellowgreen/yellow/orange) is indicating covalent interaction (green: A atoms; red: B atoms).

Single crystal preparation

Large single crystals (2 mm to 5 mm edge length) of the compounds were grown to perform measurements of some physical properties.

The crystals have been synthesized by two different methods. Antimonides and stannides were grown by dissolving the compounds in an excess of melt. The melt was then slowly cooled to room temperature. Crystals of the antimonides were isolated by sublimation of excess Sb in vacuum at 870 K. As for the stannides, the samples were cooled to 78 K. The residual tin undergoes the β- to α-phase transition and the resulting fine tin powder could easily be separated from the crystals. A large cylindrical single crystal (∅ 7 mm, length 75 mm) of

$CuAl_2$ has been grown from the stoichiometric melt of the elements using the Bridgman method.

The crystal structures of $TiSb_2$, VSb_2, $MnSn_2$, $FeSn_2$ and $CuAl_2$ were reinvestigated using the single crystals obtained and the structural data were used for quantum chemical calculations.

Quantum chemical calculations

In order to investigate the spatial arrangement of covalent interactions in the different intermetallic compounds and thus, being able to select an appropriate description, a bonding analysis of the compounds has been performed using the electron localization function (ELF) implemented in the TB-LMTO-ASA program package [1]. The results of the calculations were rather unexpected. Instead of one bonding topology, the calculations reveal three different topologies depending on the ***B*** metal involved.

In the antimonides, a strong bonding (meaning high electron numbers in the basin) is observed along the ***d***1 distance thus, Sb_2 dumbbells are formed (Fig. 2a). Weaker covalent bonds are observed between the ***A*** atoms along the ***c*** direction of the unit cell. Between the Sb atoms and the ***A*** atoms three-center bonds ***A-B-A*** are observed (Fig. 2b).

In the stannides, there are additional two-center bonds observed along the distance ***d***2 (Fig. 2c). $CuAl_2$ itself shows similar covalent interactions as the stannides except for the missing Cu-Cu interaction (Fig. 2a).

By comparing the results of the calculations with the three representations of the $CuAl_2$ structure, the picture with interpenetrating graphite-like nets representation is favored because the strong covalent bonds ***d***1 and ***d***2 are confirmed by the calculations.

Raman spectroscopy

An experimental method to get information of covalent type of bonding in a compound is optical vibration spectroscopy.

For the first time it has been possible to realize a complete symmetry assignment with polarized Raman measurements on oriented single crystals of the intermetallic compounds VSb_2, $MnSn_2$ and $CuAl_2$ (Fig. 3). According to group theoretical considerations, compounds which crystallize in the $CuAl_2$ structure type give rise to five Raman active optical modes (1 A_{1g}, 1 B_{1g}, 1 B_{2g} and 2 E_g). As a crude approximation the mode with A_{1g} symmetry represents the stretching vibration of the B_2 dumbbell and thus the bond strength for the shortest distance ***d***1 between two ***B*** atoms.

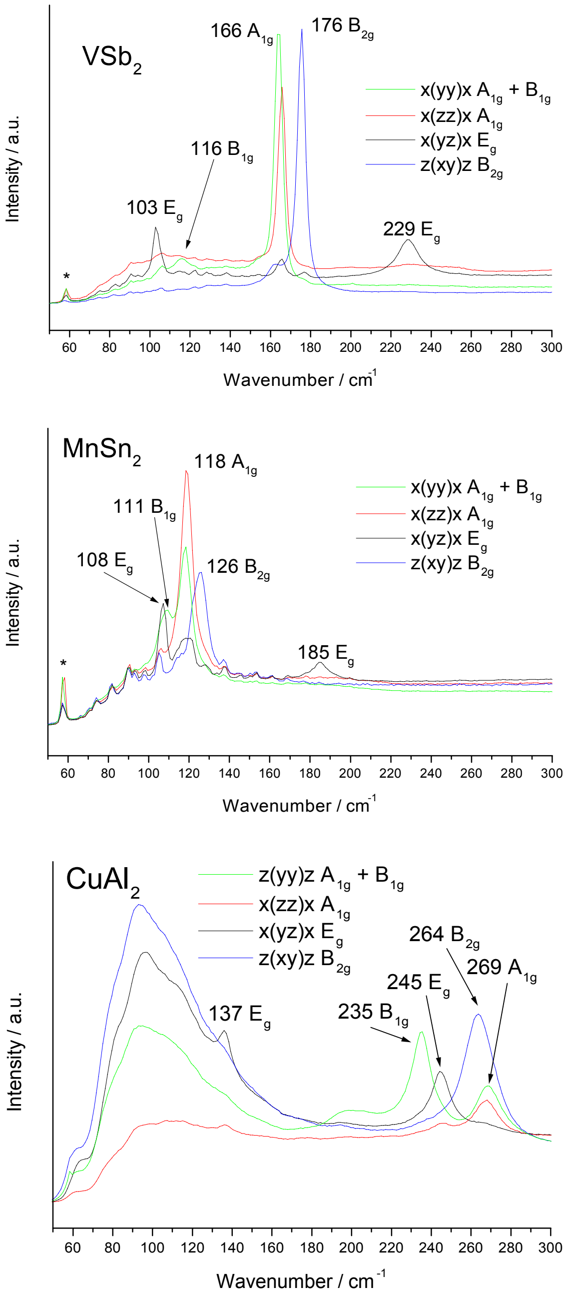

Fig. 3: Polarized Raman spectra of oriented single crystals of VSb_2 $MnSn_2$ and $CuAl_2$. In each polarized measurement only modes of a certain symmetry are allowed (* grating ghosts).

Figure 4 shows a clear correlation between the ***A***$_{1g}$ wavenumber and the $1/\chi$ values, derived from the maximal ELF value in the basin, where

$$\mathrm{ELF} = 1 / (1 + \chi^2).$$

For the first time the calculated ELF values could be related to a physical property which is indicating the bond strength between two atoms.

A correlation of $1/\chi$ and the force constant (e.g. taking the atomic masses into account) is observed for the stannides and antimonides (Fig. 4). $CuAl_2$ does not follow this correlation.

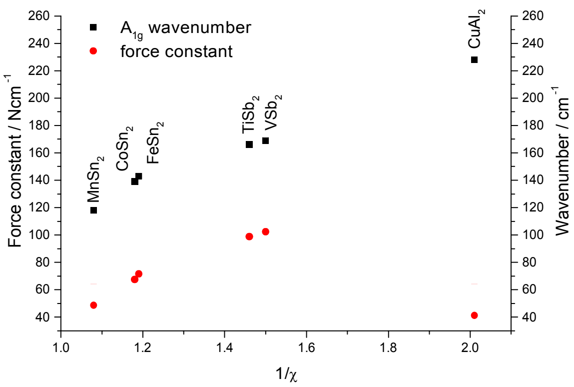

Fig. 4: Correlation between 1/χ and the wave number of the A$_{1g}$ mode the force constant as well as for representatives of the CuAl$_2$ structure type.

Hall effect and resistivity measurements

Another attempt to find an interface between experimental measurements and theoretical calculations can be made using the Hall coefficient. The measurement allows to determine the dominant kind of charge carriers for a defined direction in the compounds and their approximate number (the last only for applying a “one-band” model where one type of carriers strongly dominates the other).

To perform the direction dependent Hall effect measurements thin plates of the crystals in the different crystallographic directions are prepared by sawing and polishing.

The calculations of the Hall coefficients with the LMTO method as well as the Hall effect measurements are in progress.

Reference

[1] ***O. Jepsen, A. Burkhardt and O.K. Andersen,*** The Program TB-LMTO-ASA, Version 4.7, Max-Planck-Institut für Festkörperforschung, Stuttgart (1999).