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## Crystal Structure of New Heusler Compounds

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### Crystal Structure of New Heusler Compounds

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20 **Crystal Structure of New Heusler Compounds**  
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24 Tanja Graf, Frederick Casper, Jürgen Winterlik, Benjamin Balke, Gerhard H. Fecher,  
25  
26 and Claudia Felser\*  
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36 Received  
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38 *Dedicated to Professor Dr. Gerd Meyer on the Occasion of his 60<sup>th</sup> birthday*  
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6 **Abstract.** Heusler compounds are promising materials in many fields of contemporary  
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8 research. The spectrum of their possible applications ranges from magnetic and  
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10 magneto-mechanical materials over semiconductors and thermoelectrics to  
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12 superconductors. An important feature of the Heusler compounds is the possibility of  
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14 controlling the valence electron concentration by partial substitution of elements. On the  
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16 other hand, the properties also depend on the degree of ordering of the the crystal  
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18 structure. In general, Heusler compounds crystallize in the  $\text{Cu}_2\text{MnAl}$ -type structure but  
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20 in many cases certain types of disorder are observed. In this paper a detailed description  
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22 of the different types of disordered structures is given. Additionally, the synthesis of  
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24 new Heusler compounds is reported. The prepared compounds contain ternary Cr-, Rh-,  
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26 Ru-, Ni-, Pd-, and Pt-based Heusler systems as well as quaternary  $\text{Co}_2$ -based  
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28 compounds and compounds of the general formula  $\text{XX}'\text{YZ}$ . The crystal structure was  
29  
30 determined by XRD measurements and the structural ordering of the compounds is  
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32 discussed.  
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38 Keywords: Heusler compounds, intermetallic phases, crystal structure, X-ray diffraction  
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## 43 **Introduction**

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50 Heusler compounds are ternary intermetallics with a 2:1:1 stoichiometry [1].  
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52 They first attracted interest of the magnetism community when *Heusler et al.* [2] had  
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54 shown that the compound  $\text{Cu}_2\text{MnAl}$  becomes ferromagnetic, even though none of its  
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56 constituents is ferromagnetic by itself. However, it took three decades before their  
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6 structure was explained to be that of an ordered compound with a face centred cubic  
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8 structure [3, 4].  
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10 Interest in Heusler compounds persists since it has been established that the properties  
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12 of these intermetallic compounds can be altered by changing the degree and kind of  
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14 chemical order as well as by substituting one element by another. Co-based compounds  
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16 were synthesized and investigated in the 1970s [5]. They attracted a great deal of  
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18 interest due to their high Curie temperatures [6, 7] and being predicted to be half  
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20 metallic ferromagnets [8, 9]. Many of the Co<sub>2</sub>-based compounds are now used in  
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22 magnetic tunnel junctions [10, 11]. Today Heusler compounds have various  
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24 applications, for example they are investigated due to their properties as half-metallic  
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26 ferromagnets in the field of spintronics, thermoelectrics and superconductors [12-15].  
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### 34 **Experimental Section**

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41 Polycrystalline ingots of the compounds were prepared by arc melting of stoichiometric  
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43 amounts of high purity elements in an argon atmosphere to avoid oxygen contamination  
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45 at a pressure of 10<sup>-4</sup> mbar. Additionally, a Ti sponge was used to bind remaining oxygen.  
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47 The samples were melted three times. They were turned over after each melting process  
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49 to yield a homogeneous sample. The weight loss after the whole melting procedure was  
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51 less than 1 %. The polycrystalline ingots were annealed in an evacuated quartz tube for  
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53 one to three weeks.  
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6 The crystallographic structure was investigated by X-ray powder diffraction using  
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8 excitation by Mo  $K_{\alpha}$  radiation ( $\lambda = 0.7093165$  nm; Bruker, AXS D8) in reflection  
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10 geometry or Cu  $K_{\alpha}$  radiation ( $\lambda = 1.540598$  nm; Bruker, D5000) in transmission  
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12 geometry in a  $\theta$ - $\theta$  scanning mode. The experimental diffraction patterns were refined  
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14 using the FULLPROF program [16].  
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## 17 18 19 20 **Results and Discussion**

### 21 22 23 24 25 26 27 *Crystal Structure*

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29 The properties of Heusler compounds depend significantly upon the degree and type of  
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31 chemical order. In general,  $X_2YZ$  Heusler compounds crystallize in the cubic  $\text{Cu}_2\text{MnAl}$   
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33 structure (space group no. 225:  $Fm\bar{3}m$ ,  $L2_1$ ). The  $X$  and  $Y$  atoms are transition metals  
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35 and  $Z$  is a main group element. In some cases  $Y$  is replaced by a rare earth element or an  
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37 earth alkali metal. The cubic  $\text{Cu}_2\text{MnAl}$  structure consists of four interpenetrating  $fcc$   
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39 sub-lattices, two of which are equally occupied by  $X$ . These two  $X$ -site  $fcc$  sub-lattices  
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41 combine to form a simple cubic lattice. The  $Y$  and  $Z$  atoms occupy alternating the  
42  
43 centers of the simple cubic lattice. This results in a CsCl-like superstructure. The  $X$   
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45 atoms are placed on the Wyckoff position 8c (1/4, 1/4, 1/4). The  $Y$  and  $Z$  atoms are  
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47 located on 4a (0, 0, 0) and 4b (1/2, 1/2, 1/2) positions, respectively. The 4a and 4b  
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49 positions have  $O_h$  symmetry whereas the 8c position has  $T_d$  symmetry. The crystal  
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51 structure is displayed in Fig. 1. The illustration is shifted by (1/4, 1/4, 1/4) with respect  
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53 to the standard illustration of the  $Fm\bar{3}m$  cell to show the CsCl-like superstructure.  
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12 Fig. 1 shows the transition from the ordered to the most prominent disordered structures  
13 as will be explained in the following: If the *Y* and the *Z* atoms are evenly distributed, the  
14 4a and 4b positions become equivalent. This leads to a CsCl-like structure, also known  
15 as B2-type disorder. The symmetry is reduced and the resulting space group is  $Pm\bar{3}m$ .  
16  
17 The random distribution of the *X* and the *Y* or the *X* and the *Z* atoms results in the  $\text{BiF}_3$ -  
18 type disorder (Space group no. 216:  $Fm\bar{3}m$ ,  $\text{DO}_3$ ). The NaTl-type structure is  
19 observed very rarely. In this structure type the *X*-atoms which occupy one *fcc* sub-lattice  
20 are mixed with the *Y* atoms whereas the *X*-atoms on the other sub-lattice are mixed with  
21 the *Z* atoms. This kind of disorder is also known as B32a disorder (Space group no. 227,  
22  $Fd\bar{3}m$ ). The *X*-atoms are placed at the Wyckoff position 8a (0, 0, 0), the *Y* and *Z*  
23 randomly distributed at position 8b (1/2, 1/2, 1/2). In contrast to these partial disorder  
24 phenomena all positions become equivalent in the tungsten-type structure with a bcc  
25 lattice and reduced symmetry  $Im\bar{3}m$  (A2).  
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44 The cubic  $\text{X}_2\text{YZ}$  compounds are also found in the  $\text{CuHg}_2\text{Ti}$ -type structure as illustrated  
45 in Fig. 2 (note that the classification of the cubic  $\text{X}_2\text{YZ}$  compounds is sometimes not  
46 uniquely given in *Pearson's Handbook* [17]). In the  $\text{CuHg}_2\text{Ti}$ -type structure (space  
47 group no. 216:  $F\bar{4}3m$ , X) the *X* atoms do not build a simple cubic lattice but occupy  
48 the 4a and 4c Wyckoff positions at (0, 0, 0) and (1/4, 1/4, 1/4). The *Y* and *Z* atoms are  
49 located on 4b (1/2, 1/2, 1/2) and 4d (3/4, 3/4, 3/4) positions, respectively. All four  
50 positions have  $T_d$  symmetry. This structure is frequently observed if the nuclear charge  
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6 of the  $Y$  element is larger than the one of the  $X$  element from the same period  
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8 ( $Z(Y) > Z(X)$ ). The structure may also appear in compounds with transition metals from  
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10 different periods. Space group no. 216 is also observed in quaternary  
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12 noncentrosymmetric  $XX'YZ$  Heusler compounds. Every element occupies one of the  $fcc$   
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14 sublattices. The  $X$  atoms are located on the 4a sites whereas the  $X'$  atoms occupy the 4b  
15  
16 positions. The  $Y$  and  $Z$  atoms are situated at the 4c and 4d positions, respectively. The  
17  
18 prototype is  $\text{LiMgPdSn}$  (compare Fig. 2). The reviewing articles of Bacon and Plant [18]  
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20 as well as *Neumann* and *Ziebeck* [19, 20] summarize different types of disorder in  
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22 Heusler compounds.  
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29 **(Insert figure 2)**  
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34 Fig. 3 shows the group – subgroup relationship between all types of simple disorder that  
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36 are possible in the Heusler structure. The numbers after  $t$  and  $k$  indicate the index of the  
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38 reduction in symmetry. One should notice that there are 2 atoms per unit cell for the  
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40 tungsten and the  $\text{CsCl}$  structure. For all other structure types there are 16 atoms per unit  
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42 cell due the doubling of all cell axes.  
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53 Table 1 summarizes the different ordering variants of Heusler compounds. The site  
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55 occupancy is correlated with the corresponding general formula. Different notations of  
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6 the crystal structures according to the *ISCD*, the *Strukturberichte (SB)* and to *Pearson* as  
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8 well as the space group are given.  
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13 **(Insert table 1)**  
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17 Theoretical X-ray diffraction patterns of  $\text{Co}_2\text{MnSi}$  which were simulated under the  
18 assumption of different crystal structures are displayed in Fig. 4. Table 2 provides a  
19 survey of the relative intensities of the reflexions for the XRD patterns displayed in Fig.  
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25 4. The  $\text{Cu}_2\text{MnAl}$ -type structure is identified by the occurrence of the *fcc*-typical (111)  
26 and (200) reflexions and their relation to the (220) reflexion. However, the intensity of  
27 the two *fcc*-typical reflexions is very low in many of the investigated compounds. If the  
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The two *fcc*-typical reflexions is very low in many of the investigated compounds. If the  
 $\text{Cu}_2\text{MnAl}$ -type and the  $\text{BiF}_3$ -type structure are compared, a difference in the intensities  
of the (111) and (200) reflexions is evident. The  $\text{Cu}_2\text{MnAl}$  and the  $\text{CuHg}_2\text{Ti}$  structure  
are hardly distinguishable by X-ray diffraction. Much care has to be taken in the  
structural analysis, as both have general *fcc*-like symmetry. In the CsCl-type structure  
only the (111) reflexion vanishes whereas in the NaTl-type structure the (200) reflexion  
disappears. Both, the (111) and (200) reflexions vanish not only in the tungsten-type  
structure but also if all contained elements are from the same row of the periodic table  
due the nearly equal scattering factors. A small amount of disorder in an ordered  
compound or a low degree of order in a disordered structure may occur. This is not  
detectable by standard XRD. Thus, small amounts of partial disorder cannot be  
excluded without detailed analysis of further structural investigations, for example by

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6 neutron diffraction, Mössbauer spectroscopy, NMR or EXAFS, even if the XRD data  
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8 indicate the  $\text{Cu}_2\text{MnAl}$  structure.  
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13 **(Insert figure 4)**  
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18 **(Insert table 2)**  
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### 20 21 22 23 24 *Structural Characterization* 25

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27 We report on the crystal structure of newly synthesized Heusler compounds. Tables 3, 4,  
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29 and 5 provide an overview of the different types of Heusler compounds and their crystal  
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31 structure.  
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33  
34 Table 3 summarizes the prepared ternary Heusler compounds. Fig. 5 shows the XRD  
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36 results of  $\text{Cr}_2\text{CoGa}$ . The compound fulfils the criteria of  $Z(X) < Z(Y)$ . Since the (200)  
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38 reflexion is not present but the (311) reflexion is detectable, it is concluded that the  
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40 compound exhibits the  $\text{CuHg}_2\text{Ti}$  structure. The (111) reflexion cannot be detected due  
41  
42 to the fluorescence in that  $\theta$  range. For comparison the calculated diffraction pattern for  
43  
44 the  $\text{Cu}_2\text{MnAl}$ -type structure given as an inset in Fig. 5.  
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51 **(Insert figure 5)**  
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6 The Pd<sub>2</sub>-based compounds with exception of Pd<sub>2</sub>NbAl exhibit the Cu<sub>2</sub>MnAl-type  
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8 structure. The Pt<sub>2</sub>-based compounds Pt<sub>2</sub>ScSn and Pt<sub>2</sub>ZrIn exhibit the Cu<sub>2</sub>MnAl-type and  
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10 the CsCl-type structure, respectively. Ru<sub>2</sub>TiSi exhibits the Cu<sub>2</sub>MnAl structure with a  
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12 CsCl-type disorder of approximately 18%. The tungsten structure type is observed for  
13  
14 the compound Ni<sub>2</sub>MoGa (all atoms are randomly distributed).  
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18 The structural properties of quaternary Co<sub>2</sub>-based Heusler compounds with different  
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20 substitutions on the Y or Z side are given in Table 4. Fig. 6 displays the powder XRD  
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22 pattern of Co<sub>2</sub>Mn<sub>0.95</sub>Sc<sub>0.05</sub>Ga measured with Mo K<sub>α</sub> radiation. The result of the  
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24 refinement and the difference between refinement and measurement are included in the  
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26 figure. The diffraction pattern exhibits only the (220) reflexion. This is caused by the  
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28 low intensity of the (111) and (200) reflexions mentioned above. Typically all  
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30 compounds containing solely elements from one row show only the cubic main  
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32 reflexions by regular XRD measurements. The crystal structure of these compounds  
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34 cannot be clearly determined by regular XRD measurements. For this reason the  
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36 structure is denoted as "cubic" in the classification in Table 4. Co<sub>2</sub>MnGa<sub>0.5</sub>Si<sub>0.5</sub> and  
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38 Co<sub>2</sub>MnAl<sub>0.5</sub>Ge<sub>0.5</sub> exhibit only the (200) reflexion. Thus the XRD data indicate a CsCl-  
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40 type structure. Due to its weak intensity the (111) reflexion cannot be observed. The  
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42 Cu<sub>2</sub>MnAl-type structure may exist but cannot be confirmed by analysis using standard  
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44 XRD methods. The remaining compounds mentioned in Table 4 exhibit the Cu<sub>2</sub>MnAl-  
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46 type structure.  
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10 Fig. 7 shows the refined powder XRD pattern of NiCuScAl. The data indicate the  
11 Cu<sub>2</sub>MnAl-type structure according to the explanation above. This structure corresponds  
12 to the general formula (Ni<sub>0.5</sub>Cu<sub>0.5</sub>)<sub>2</sub>ScAl with an equal distribution of Ni and Cu on the  
13 X sides. Since the relation of intensities is correct a significant amount of disorder in the  
14 compound can be excluded. However, it has to be mentioned that the data do not  
15 provide the information if the compound crystallizes in the LiMgPdSn structure which  
16 means that the Ni and Cu atoms are ordered on separate sublattices. This better ordered  
17 structure corresponds to the general formula NiCuScAl. Similar structural properties are  
18 observed for all other quaternary compounds listed in Table 5. These compounds are  
19 classified as crystallizing in the Cu<sub>2</sub>MnAl-type structure although the LiMgPdSn-type  
20 structure might be present.  
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38 **(Insert figure 7)**  
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## 50 **Conclusion**

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55 Several new Heusler compounds have been synthesized and analysed by the means of  
56 X-ray diffraction. Different types of disorder that occur in this structure type have been  
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6 found. On the other hand it should be noted that it is hard to distinguish between some  
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8 disorder types with regular XRD methods. As the magnetic and electronic properties of  
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10 Heusler compounds depend on the crystalline structure, these compounds should be  
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12 investigated by many structure sensitive analysing methods.  
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26 gratefully acknowledged.  
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## References

- [1] F. Heusler, *Verh. DPG* **1903**, 5, 219.
- [2] F. Heusler, W. Starck, E. Haupt, *Verh. DPG* **1903**, 5, 220.
- [3] O. Heusler, *Ann. Phys.* **1934**, 411, 155.
- [4] A. J. Bradley; J. W. Rodgers, *Proc. R. Soc.* **1934**, 144, 340.
- [5] P. J. Webster, *J. Phys. Chem. Solids* 1971, 32, 1221.
- [6] S. Wurmehl, G. H. Fecher, V. Ksenofontov, F. Casper, U. Stumm, C. Felser, *J. Appl. Phys.* **2006**, 99, 08J103.
- [7] S. Wurmehl, G. H. Fecher, H. C. Kandpal, V. Ksenofontov, C. Felser, *Appl. Phys. Lett.* **2006**, 86, 032502.
- [8] J. Kübler, A. R. William, C. B. Sommers, *Phys. Rev. B* **1983**, 28, 1745.
- [9] R. A. de Groot, F. M. Müller, P. G. van Engen, K. H. J. Buschow, *Phys. Rev. Lett.* **1983**, 50, 2024.
- [10] T. Marukame, T. Ishikawa, S. Hakamata, K. Matsuda, T. Urmura, M. Yamamoto, *Appl. Phys. Lett.* **2007**, 90, 012580.
- [11] N. Tezuka, N. Ikeda, S. Sugimoto, K. Inomata, *Appl. Phys. Lett.* **2006**, 89, 252508.
- [12] N. Shutoh, S. Sakurada, *J. Alloys Compds.* **2005**, 389, 204.
- [13] I. Galanakis, P. H. Dederichs, N. Papanikolaou, *Phys. Rev. B* **2002**, 66, 174429.
- [14] C. Felser, G. H. Fecher, B. Balke, *Angew. Chem.* **2007**, 46, 668.

- 1  
2  
3  
4  
5  
6 [15] J. Winterlik, G. H. Fecher, C. Felser, *Solid State Commun.* **2008**, 145, 475.  
7  
8  
9 [16] J. Rodríguez-Carvajal, *Physica B* **1993**, 192, 55.  
10  
11 [17] L. C. P. Villars, *Pearson's Handbook of Crystallographic Data for Intermetallic*  
12 *Phases*, 2<sup>nd</sup>. ed., Materials Park, OH: ASM International 1991.  
13  
14  
15  
16 [18] G. E. Bacon, J. S. Plant, *J. Phys. F: Metal Phys.* **1971**, 524.  
17  
18  
19 [19] P. J. Webster, K. R. A. Ziebeck, *Landolt-Brönstein-Group III Condensed Matter*  
20 **1988**, 19c, 75.  
21  
22  
23  
24 [20] K. R. A. Ziebeck, K. U. Neumann, *Landolt-Brönstein-Group III Condensed Matter*  
25 **2001**, 32c, 64.  
26  
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## Figure Captions

Fig. 1

Crystal structures of the  $X_2YZ$  Heusler compounds.

The  $Cu_2MnAl$  ( $L2_1$ ) structure and preferential types of disorder: The  $BiF_3$  ( $DO_3$ ),  $CsCl$  ( $B2$ ) and Tungsten ( $A2$ ) structure. Note that all positions are shifted by  $(1/4, 1/4, 1/4)$  with respect to the standard  $Fm\bar{3}m$  cell to make the  $CsCl$  superstructure visible.

Fig. 2

Crystal structure of the Heusler compounds in space group  $F\bar{4}3m$ .

The  $CuHg_2Ti$ -structure and the noncentrosymmetric  $LiMgPdSn$ -structure of  $XX'YZ$  compounds.

Fig. 3

Bärninghaus tree of the group-subgroup relationship of the Heusler structure and its disorder variants. The indices of *klassengleiche* (k) and *translationsgleiche* (t) as well as the unit cell transformations and the origin shifts are given.

Fig. 4

Simulated X-ray diffraction patterns measured with  $Mo K_\alpha$  radiation for  $Co_2MnSi$  in different crystal structures: a)  $Cu_2MnAl$ -type ( $L2_1$ ), b)  $CsCl$ -type ( $B2$ ), c)  $BiF_3$ -type ( $DO_3$ ), d) tungsten-type ( $A2$ ), e)  $CuHg_2Ti$ -type ( $X$ ) and f)  $NaTl$ -type ( $B32a$ ) structure.

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6 Fig. 5  
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8 X-ray diffraction pattern of  $\text{Cr}_2\text{CoGa}$  measured with  $\text{Cu K}_\alpha$  radiation.  
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10 The compound exhibits the  $\text{CuHg}_2\text{Ti}$ -type structure. For comparison the theoretical  
11 diffraction pattern of the  $\text{Cu}_2\text{MnAl}$ -type structure is displayed as an inset.  
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18 Fig. 6  
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20 XRD pattern of  $\text{Co}_2\text{Mn}_{0.95}\text{Sc}_{0.05}\text{Ga}$  measured with  $\text{Mo K}_\alpha$  radiation.  
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22 Although the diffraction pattern shows the typical features of the tungsten-type structure,  
23 the degree of order cannot be determined since the intensity of the *fcc*-typical (111) and  
24 (220) reflexions is too weak.  
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32 Fig. 7  
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34 XRD pattern of  $\text{NiCuScIn}$  measured with  $\text{Mo K}_\alpha$  radiation. The diffraction pattern  
35 shows the typical features of the  $\text{Cu}_2\text{MnAl}$  structure, the superlattice reflexions (111)  
36 and (200) are present. A differentiation between the  $\text{Cu}_2\text{MnAl}$  and the  $\text{LiMgPdSn}$   
37 structure is not possible since the calculated XRD patterns of these two structures are  
38 almost identical.  
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10 Table 1

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12 Relation between ordered – disordered Heusler structures and different forms of  
13 notations.  
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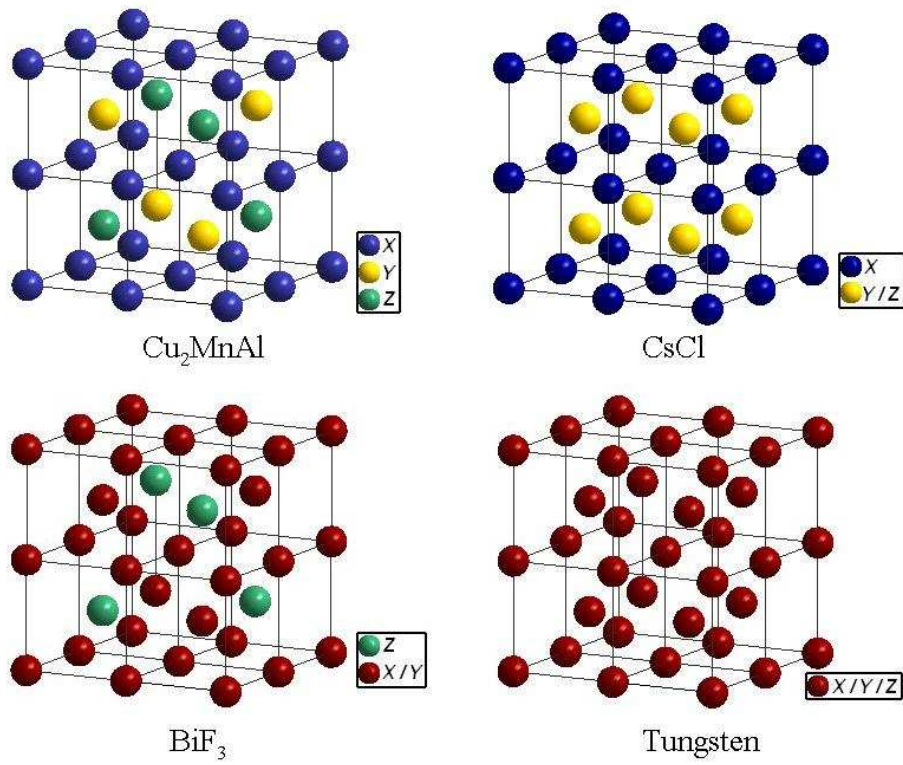


Fig. 1

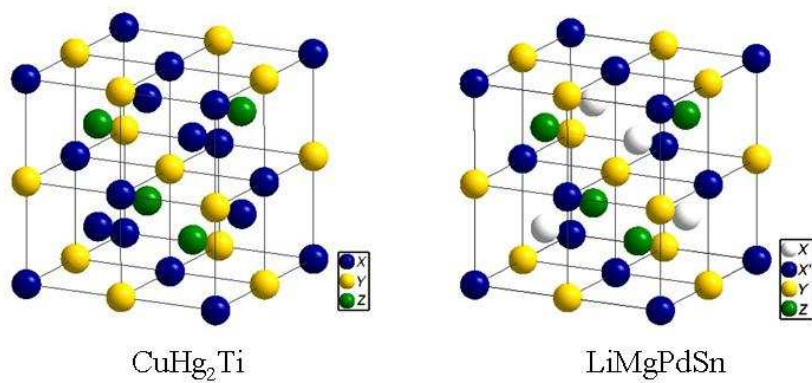


Fig. 2

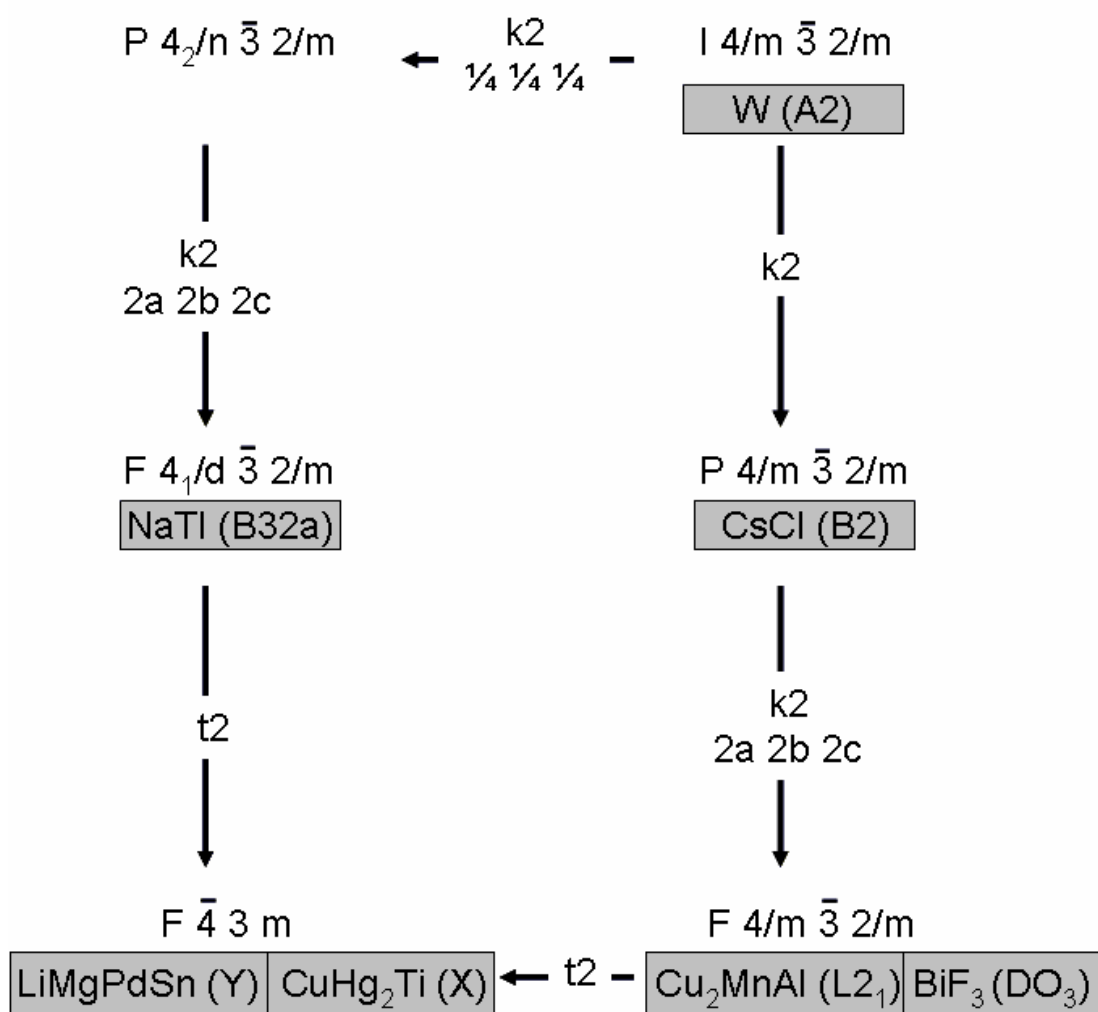


Fig. 3

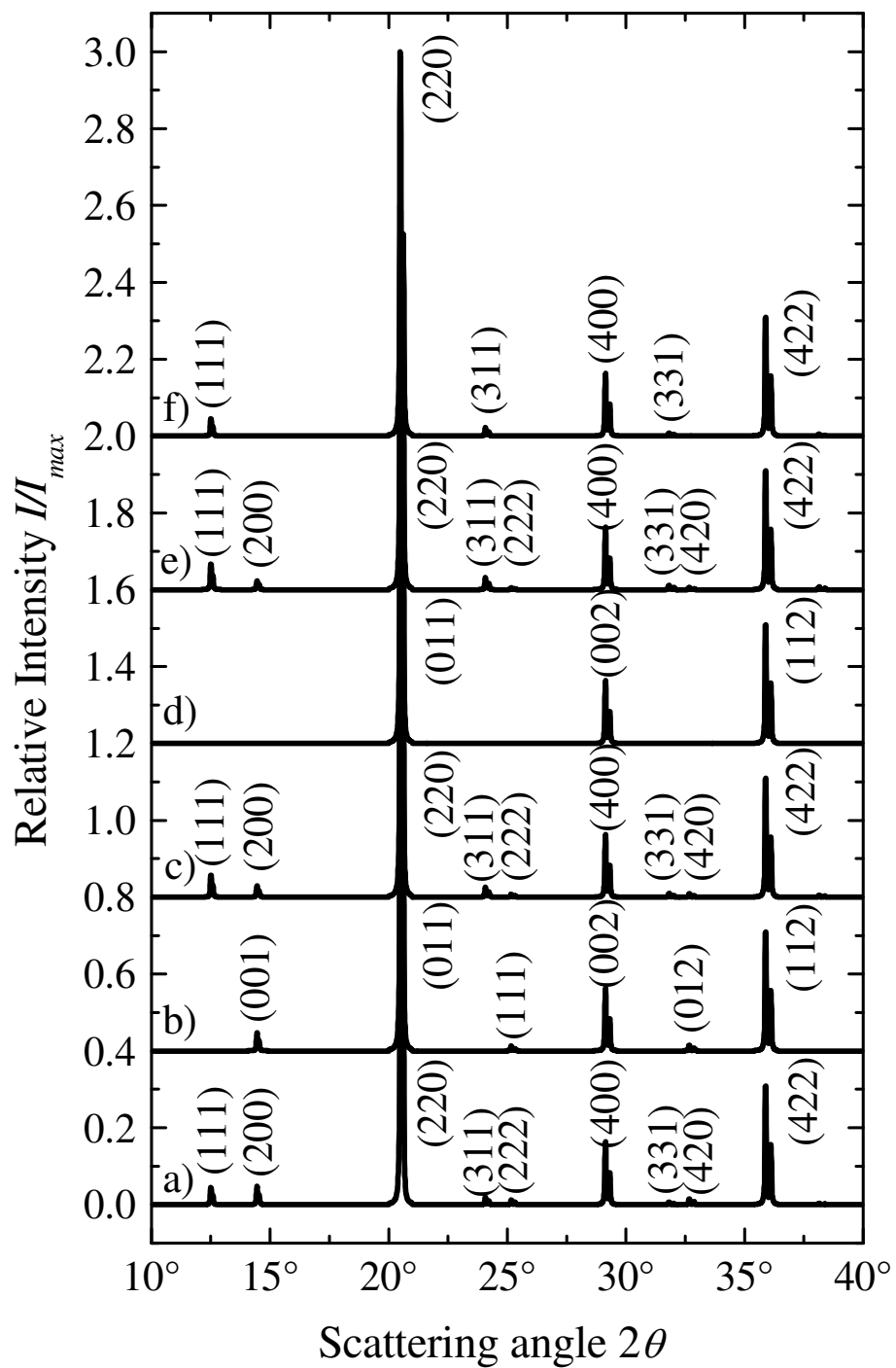


Fig. 4

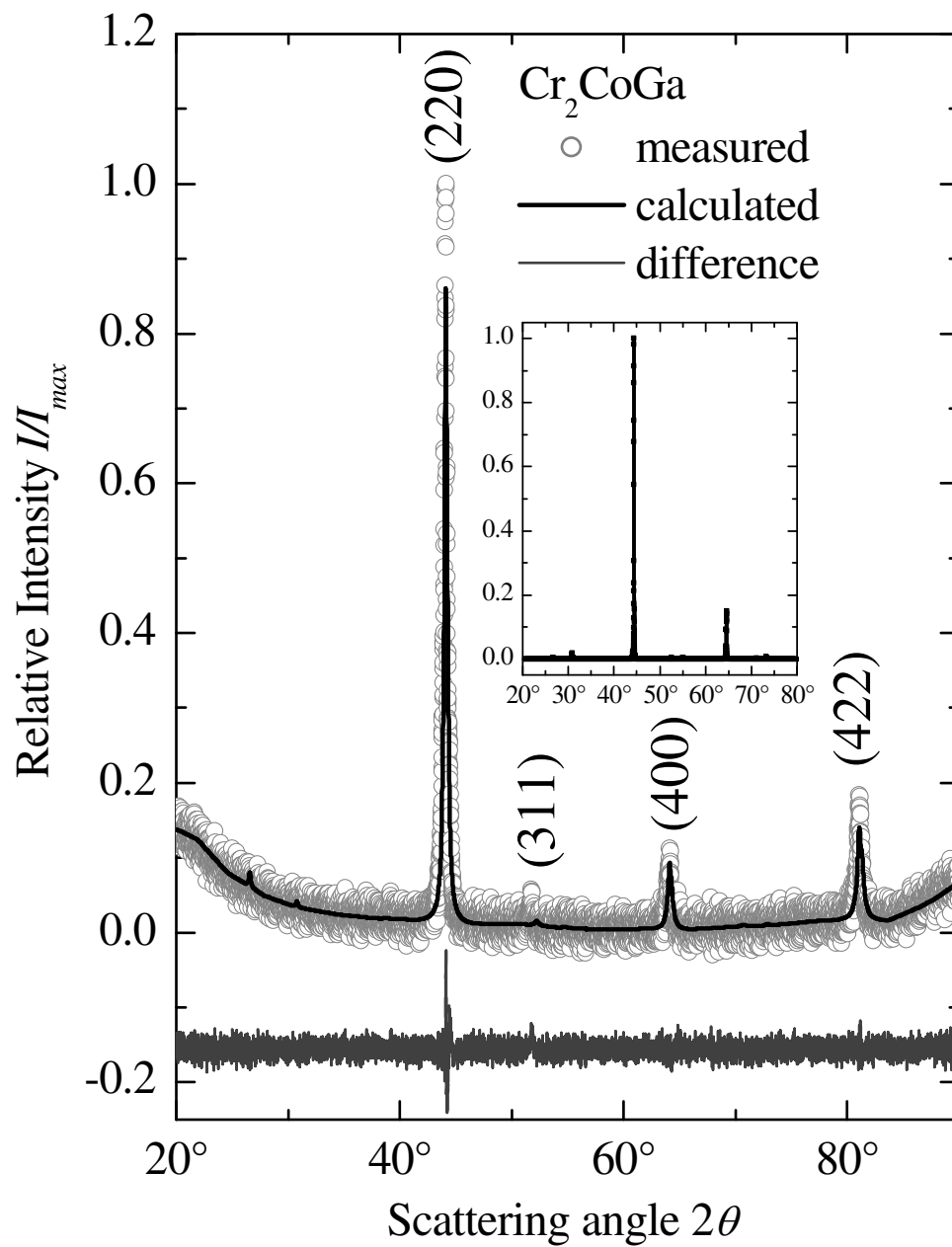


Fig. 5

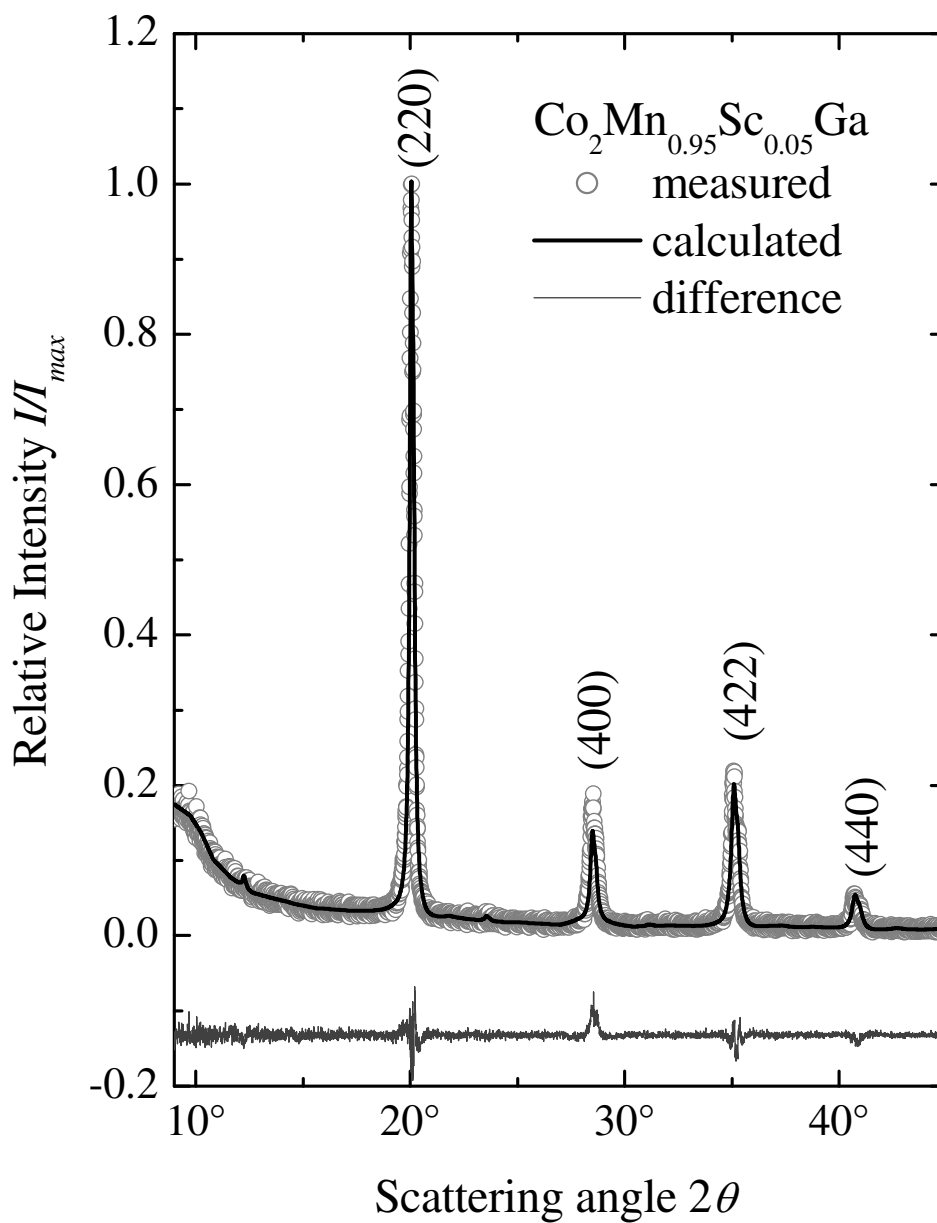


Fig. 6

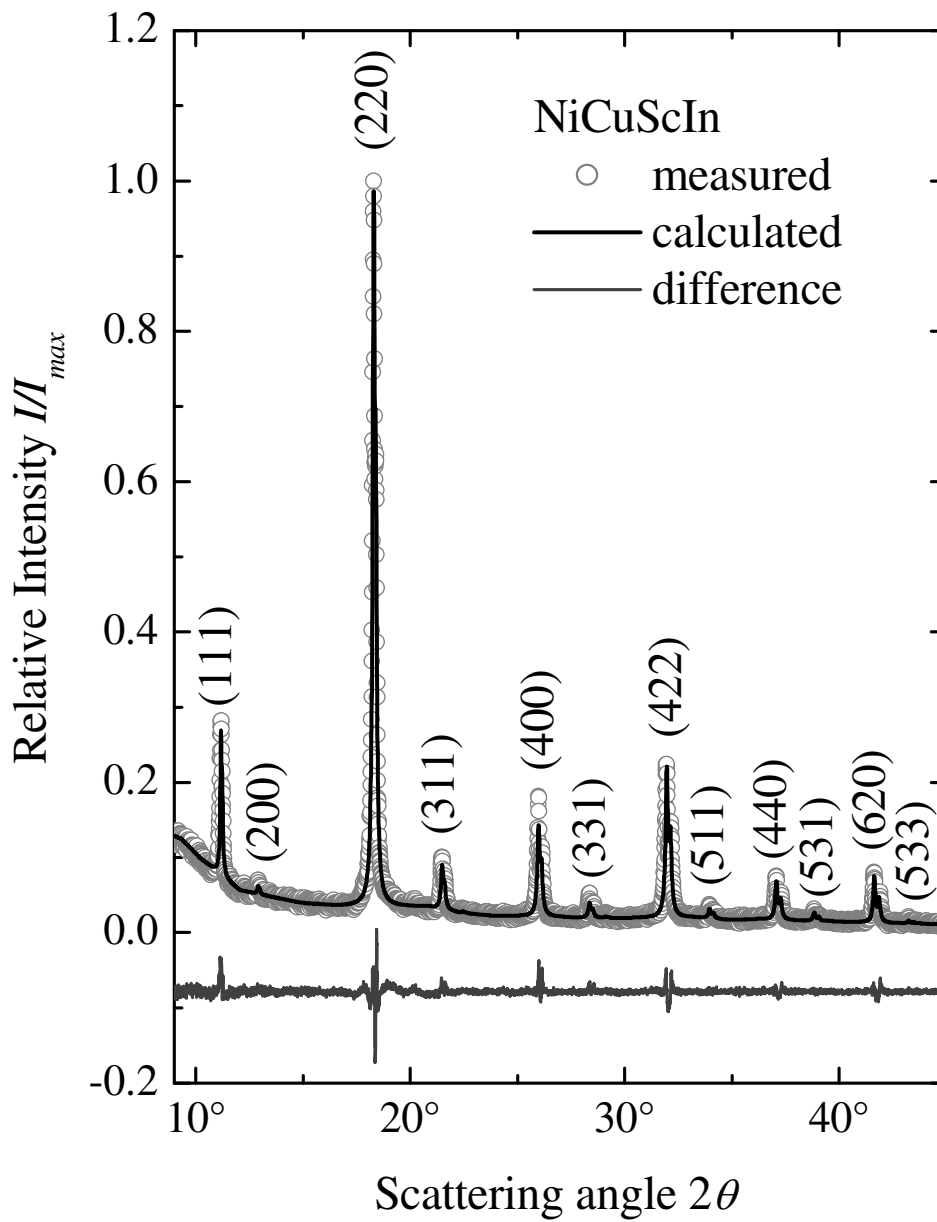


Fig. 7

site occupancy	general formula	structure type ICSD	SB	space group	Pearson
$X, X', Y, Z$	$XX'YZ$	LiMgPdSn	Y	$F \bar{4} 3m$ (no. 216)	cF16
$X=X, Y, Z'$	$X_2YZ$	Cu <sub>2</sub> MnAl	L2 <sub>1</sub>	$F m \bar{3} m$ (no. 225)	cF16
$X, X'=Y, Z$	$XX'_2Z$	CuHg <sub>2</sub> Ti	X	$F \bar{4} 3m$ (no. 216)	cF16
$X=X'=Y, Z$	$X_3Z$	BiF <sub>3</sub>	DO <sub>3</sub>	$F m \bar{3} m$ (no. 225)	cF16
$X=X', Y=Z$	$X_2Y_2$	CsCl	B2	$P m \bar{3} m$ (no. 221)	cP2
$X=Y, X'=Z$	$X_2X'_2$	NaTl	B32a	$F d \bar{3} m$ (no. 227)	cF16
$X=X'=Y=Z$	$X_4$	W	A2	$I m \bar{3} m$ (no. 229)	cI2

Table 1

Structure	(111)	(200)	(220)	(311)	(222)	(400)
Cu <sub>2</sub> MnAl	4.30	4.67	100	2.01	1.30	16.46
CsCl	-	4.67	100	-	1.30	16.46
BiF <sub>3</sub>	0.79	0.41	100	0.33	0.09	16.58
Tungsten	-	-	100	-	-	16.58
CuHg <sub>2</sub> Ti	6.53	2.27	100	3.26	0.57	16.46
NaI	4.38	-	100	2.26	-	16.46

Table 2

Compound	Structure	a / Å
Cr <sub>2</sub> CoGa	CuHg <sub>2</sub> Ti	5.81
Ni <sub>2</sub> MgSb	Cu <sub>2</sub> MnAl	6.06
Ni <sub>2</sub> MoGa	W	6.25
Pd <sub>2</sub> HfGa	Cu <sub>2</sub> MnAl	6.34
Pd <sub>2</sub> NbAl	CsCl	6.47
Pd <sub>2</sub> MgSb	Cu <sub>2</sub> MnAl	6.46
Pd <sub>2</sub> MoAl	Cu <sub>2</sub> MnAl	6.27
Pd <sub>2</sub> ZrSn	Cu <sub>2</sub> MnAl	6.55
Pt <sub>2</sub> ScSn	Cu <sub>2</sub> MnAl	6.54
Pt <sub>2</sub> ZrIn	CsCl <sup>1)</sup>	6.56
Ru <sub>2</sub> TiSi	Cu <sub>2</sub> MnAl	5.95

<sup>1)</sup> The Cu<sub>2</sub>MnAl-type structure is possible but the (111) reflexion is not detectable due to the low scattering intensity.

Table 3

Compound	Structure	a / Å
Co <sub>2</sub> Fe <sub>0.76</sub> Sc <sub>0.24</sub> Ga	cubic	5.73(6)
Co <sub>2</sub> Fe <sub>0.7</sub> Ti <sub>0.3</sub> Ga	cubic	5.77(5)
Co <sub>2</sub> Fe <sub>0.45</sub> Ti <sub>0.55</sub> Ge	Cu <sub>2</sub> MnAl	5.79(1)
Co <sub>2</sub> Fe <sub>0.6</sub> V <sub>0.4</sub> Ga	cubic	5.75(9)
Co <sub>2</sub> MnAl <sub>0.5</sub> Ge <sub>0.5</sub>	CsCl <sup>2)</sup>	5.75(1)
Co <sub>2</sub> MnAl <sub>0.5</sub> Si <sub>0.5</sub>	Cu <sub>2</sub> MnAl	5.70(1)
Co <sub>2</sub> Mn <sub>0.5</sub> Fe <sub>0.5</sub> Sn	Cu <sub>2</sub> MnAl	5.96(3)
Co <sub>2</sub> Mn <sub>0.5</sub> V <sub>0.5</sub> Si	Cu <sub>2</sub> MnAl	5.65(3)
Co <sub>2</sub> MnGa <sub>0.5</sub> Ge <sub>0.5</sub>	Cu <sub>2</sub> MnAl	5.76(1)
Co <sub>2</sub> MnGa <sub>0.5</sub> Si <sub>0.5</sub>	CsCl <sup>2)</sup>	5.70(9)
Co <sub>2</sub> Mn <sub>0.95</sub> Sc <sub>0.05</sub> Ga	cubic	5.76(5)
Co <sub>2</sub> Mn <sub>0.7</sub> Sc <sub>0.3</sub> Sn	Cu <sub>2</sub> MnAl	6.00(7)
Co <sub>2</sub> Mn <sub>0.935</sub> Ti <sub>0.065</sub> Ga	cubic	5.80(8)
Co <sub>2</sub> Mn <sub>0.6</sub> Ti <sub>0.4</sub> Ge	Cu <sub>2</sub> MnAl	5.77(1)
Co <sub>2</sub> Mn <sub>0.9</sub> V <sub>0.1</sub> Ga	cubic	5.80(3)
Co <sub>2</sub> Ti <sub>0.5</sub> Fe <sub>0.5</sub> Si	Cu <sub>2</sub> MnAl	5.67(8)
Co <sub>2</sub> Ti <sub>0.5</sub> Fe <sub>0.5</sub> Sn	Cu <sub>2</sub> MnAl	6.05(3)
Co <sub>2</sub> Ti <sub>0.5</sub> Mn <sub>0.5</sub> Si	Cu <sub>2</sub> MnAl	5.70(6)
Co <sub>2</sub> Ti <sub>0.5</sub> Mn <sub>0.5</sub> Sn	Cu <sub>2</sub> MnAl	6.03(3)

$\text{Co}_2\text{Ti}_{0.5}\text{V}_{0.5}\text{Sn}$	$\text{Cu}_2\text{MnAl}$	5.98(5)
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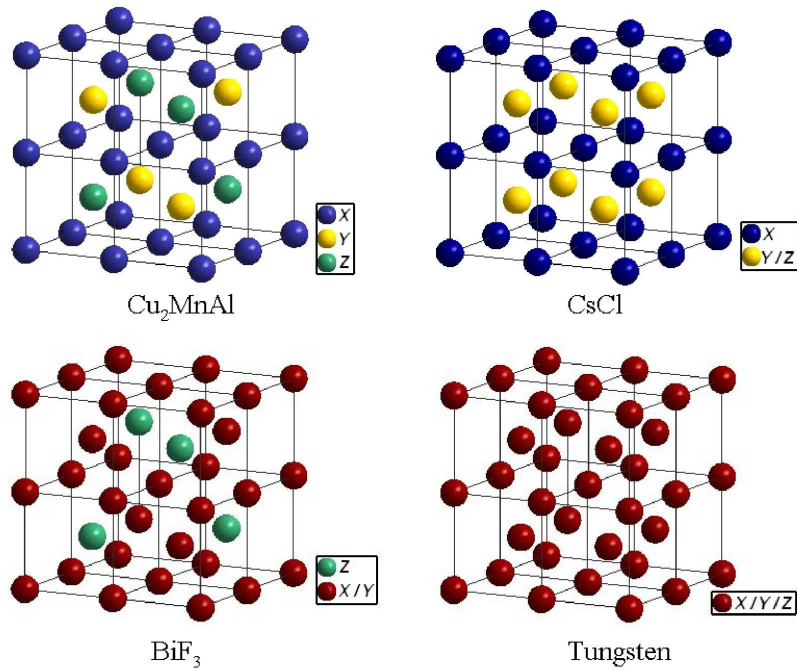
<sup>2</sup>) The  $\text{Cu}_2\text{MnAl}$ -type structure is possible but the (111) reflexion is not detectable due to the low scattering intensity.

#### Table 4

Compound	Structure <sup>3)</sup>	a / Å
(Ni <sub>0.5</sub> Ag <sub>0.5</sub> ) <sub>2</sub> ScAl	Cu <sub>2</sub> MnAl	6.52
(Ni <sub>0.5</sub> Cu <sub>0.5</sub> ) <sub>2</sub> ScAl	Cu <sub>2</sub> MnAl	6.16
(Ni <sub>0.5</sub> Cu <sub>0.5</sub> ) <sub>2</sub> ScGa	Cu <sub>2</sub> MnAl	6.05
(Ni <sub>0.5</sub> Cu <sub>0.5</sub> ) <sub>2</sub> ScIn	Cu <sub>2</sub> MnAl	6.30
(Pd <sub>0.5</sub> Ag <sub>0.5</sub> ) <sub>2</sub> ScAl	Cu <sub>2</sub> MnAl	6.48
(Pd <sub>0.5</sub> Ag <sub>0.5</sub> ) <sub>2</sub> ScIn	Cu <sub>2</sub> MnAl	6.58
(Pd <sub>0.5</sub> Ag <sub>0.5</sub> ) <sub>2</sub> YIn	Cu <sub>2</sub> MnAl	6.79
(Pd <sub>0.5</sub> Au <sub>0.5</sub> ) <sub>2</sub> ScIn	Cu <sub>2</sub> MnAl	6.57

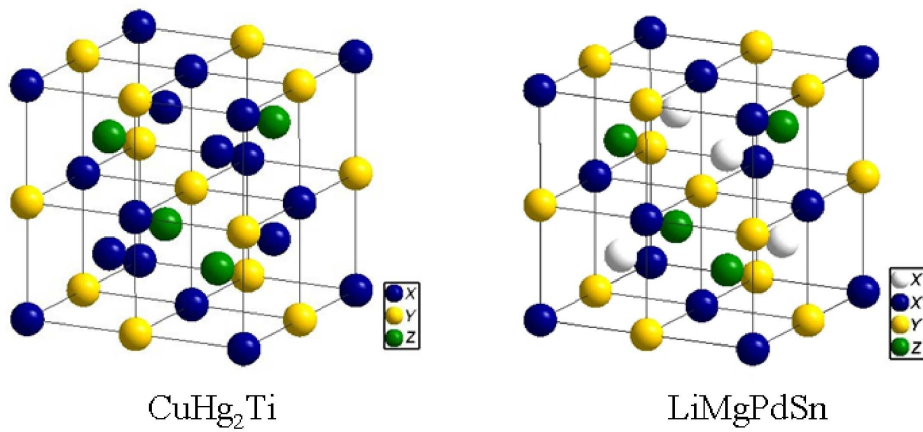
<sup>3)</sup> The XRD pattern of the structure LiMgPdSn does not differ significantly from one of the Cu<sub>2</sub>MnAl structure. Therefore it is not possible to determine whether the compounds are ordered at X and X' positions.

Table 5

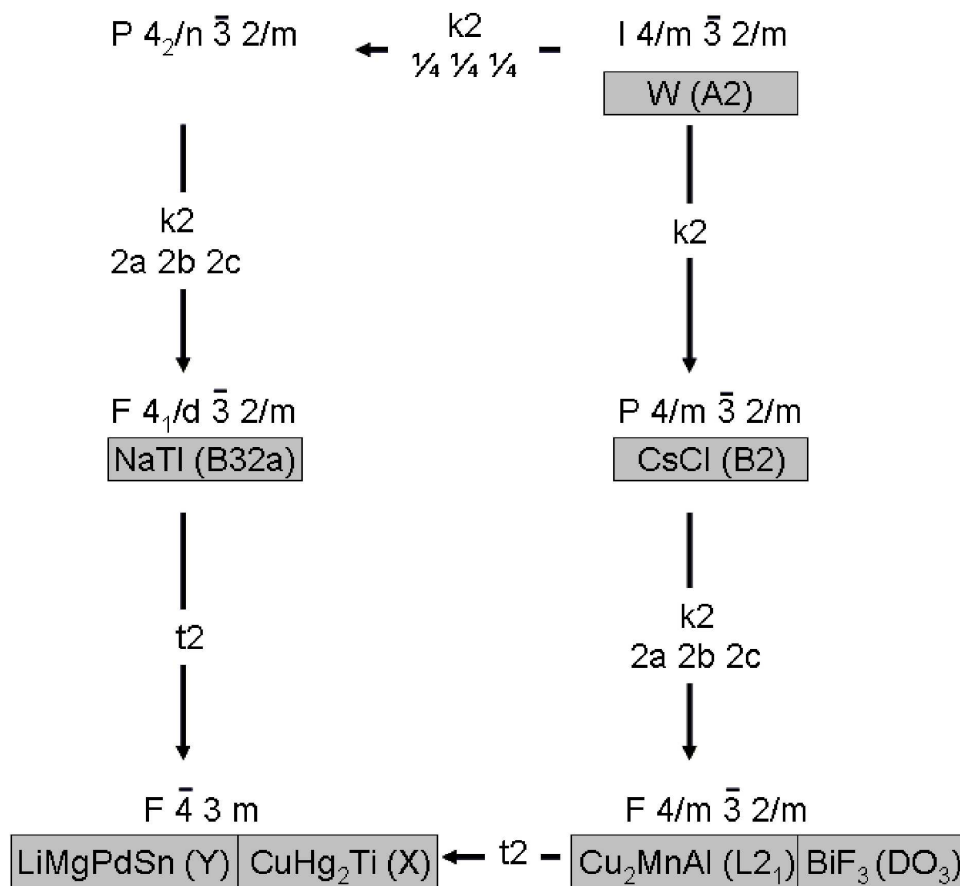


Crystal structures of the X<sub>2</sub>YZ Heusler compounds. The Cu<sub>2</sub>MnAl (L2<sub>1</sub>) structure and preferential types of disorder: The BiF<sub>3</sub> (DO<sub>3</sub>), CsCl (B2) and Tungsten (A<sub>2</sub>) structure. Note that all positions are shifted by (1/4, 1/4, 1/4) with respect to the standard F m m cell to make the CsCl superstructure visible.

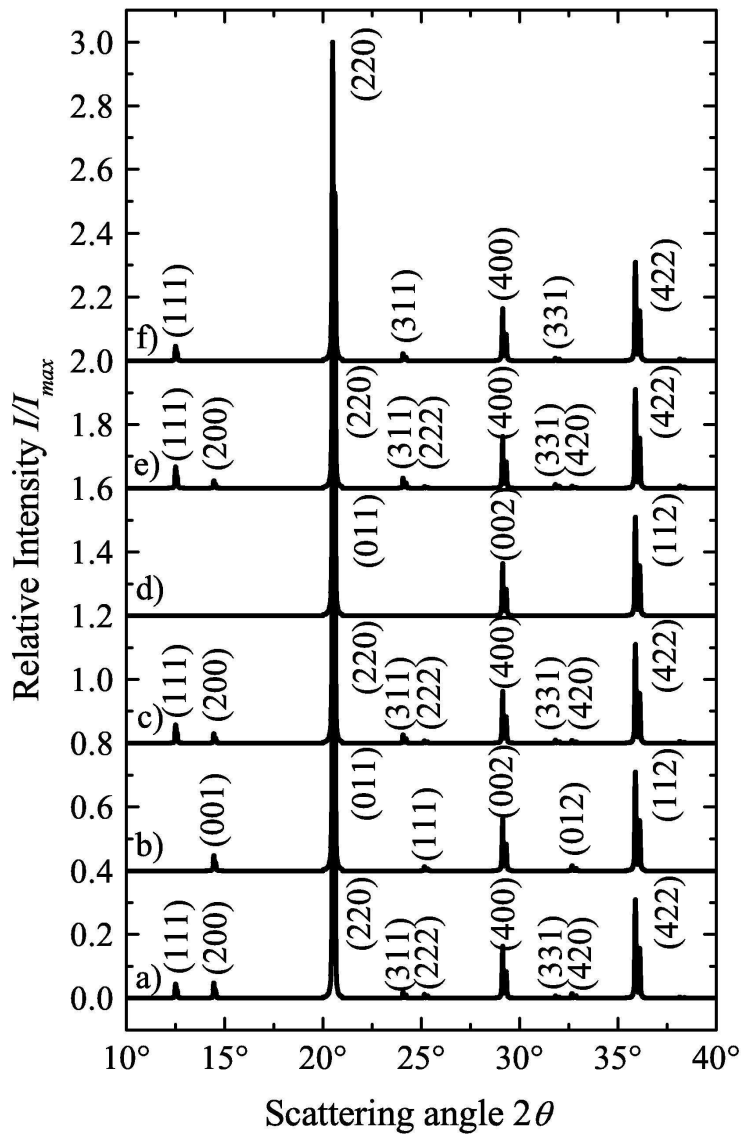
254x190mm (600 x 600 DPI)



Crystal structure of the Heusler compounds in space group  $F\bar{3}m$ . The  $\text{CuHg}_2\text{Ti}$ -structure and the noncentrosymmetric  $\text{LiMgPdSn}$ -structure of  $\text{XX}'\text{YZ}$  compounds.  
196x91mm (600 x 600 DPI)

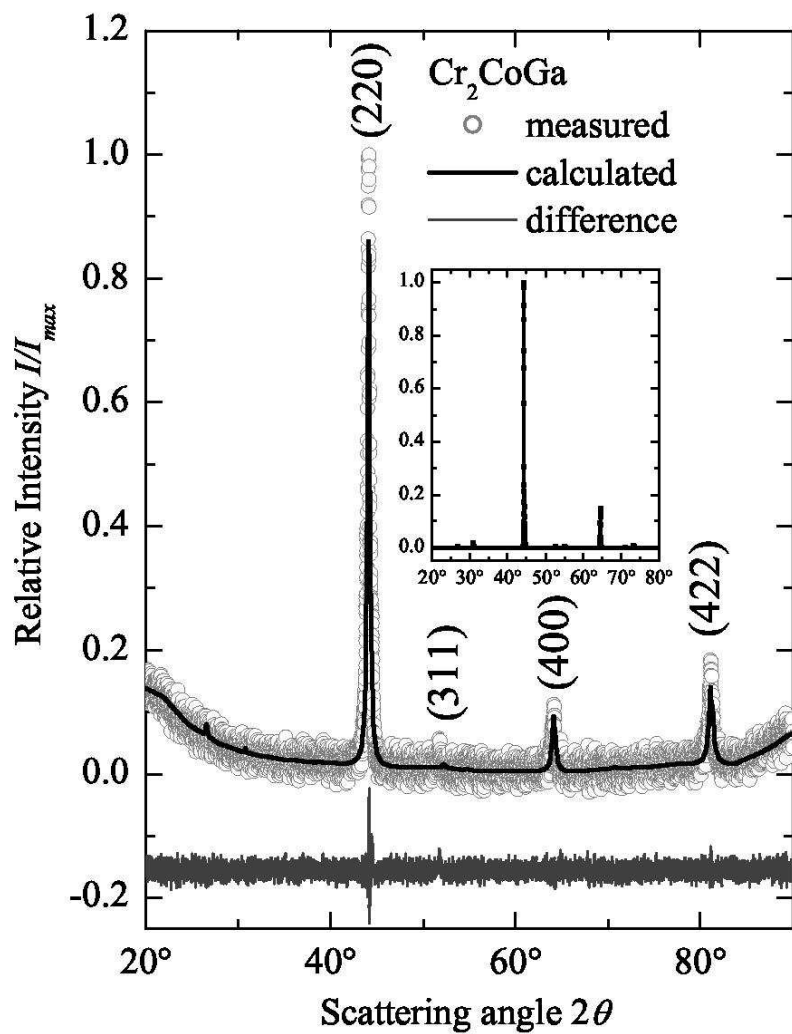


Bärninghaus tree of the group-subgroup relationship of the Heusler structure and its disorder variants. The indices of klassengleiche (k) and translationsgleiche (t) as well as the unit cell transformations and the origin shifts are given.  
247x233mm (600 x 600 DPI)



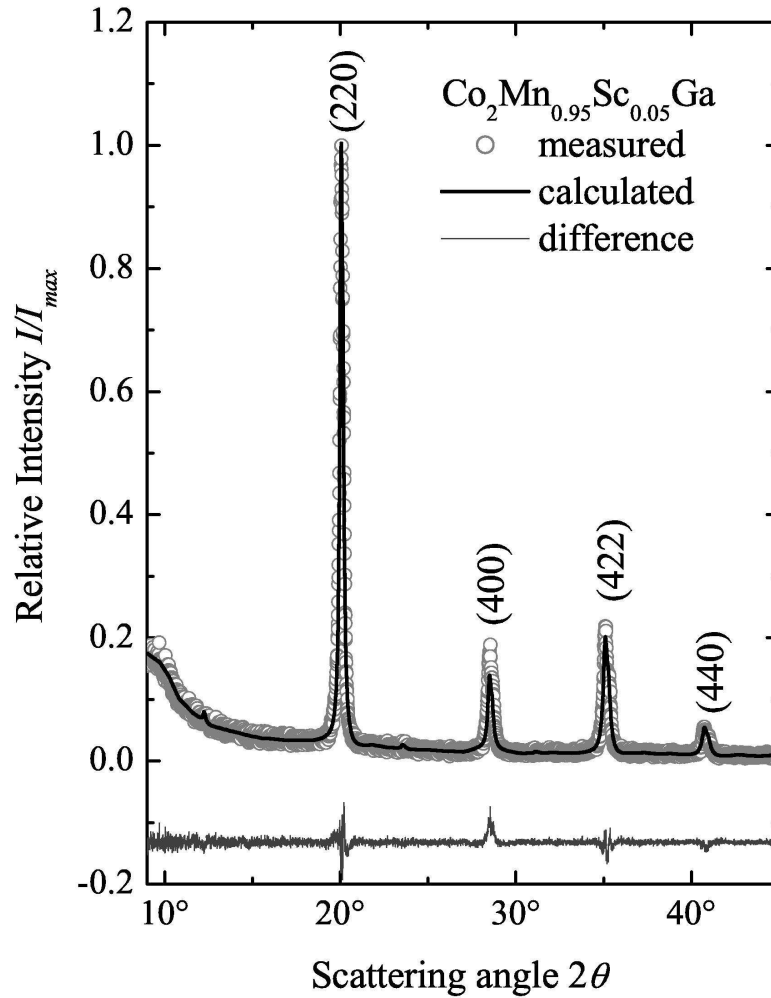
Simulated X-ray diffraction patterns measured with Mo  $K\alpha$  radiation for Co<sub>2</sub>MnSi in different crystal structures: a) Cu<sub>2</sub>MnAl-type (L21), b) CsCl-type (B2), c) BiF<sub>3</sub>-type (DO<sub>3</sub>), d) tungsten-type (A<sub>2</sub>), e) CuHg<sub>2</sub>Ti-type (X) and f) NaTi-type (B<sub>32a</sub>) structure.

81x115mm (600 x 600 DPI)



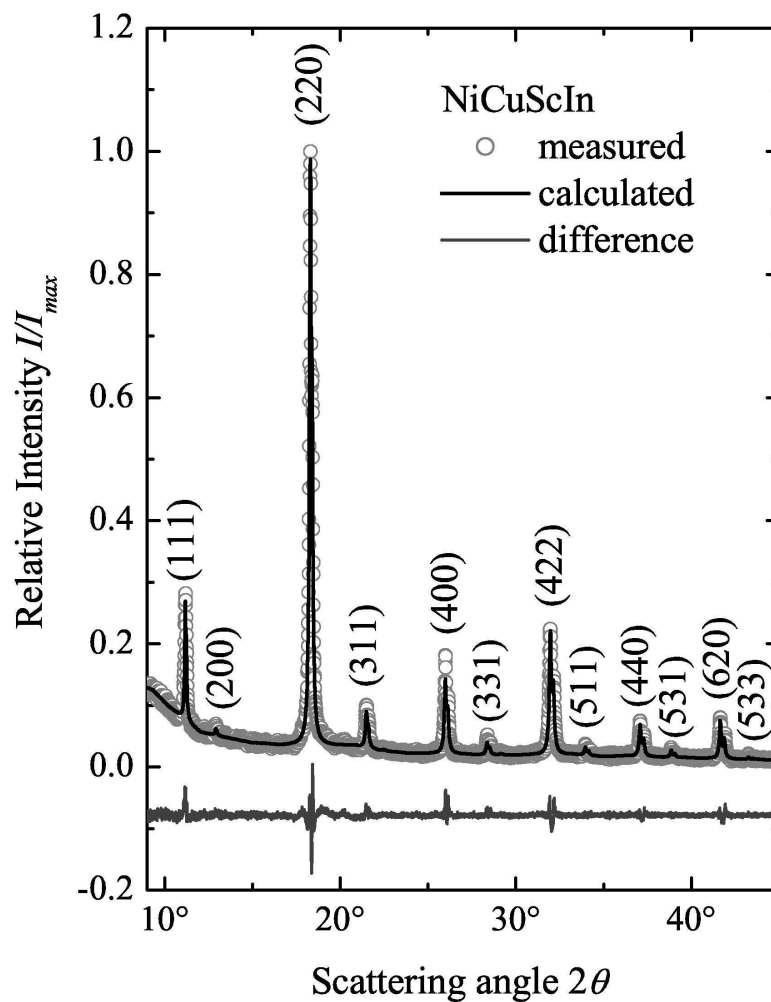
X-ray diffraction pattern of Cr<sub>2</sub>CoGa measured with Cu K $\alpha$  radiation. The compound exhibits the CuHg<sub>2</sub>Ti-type structure. For comparison the theoretical diffraction pattern of the Cu<sub>2</sub>MnAl-type structure is displayed as an inset.

43x56mm (600 x 600 DPI)



XRD pattern of Co<sub>2</sub>Mn<sub>0.95</sub>Sc<sub>0.05</sub>Ga measured with Mo  $K\alpha$  radiation. Although the diffraction pattern shows the typical features of the tungsten-type structure, the degree of order cannot be determined since the intensity of the fcc-typical (111) and (220) reflexions is too weak.

86x111mm (600 x 600 DPI)



XRD pattern of NiCuScIn measured with Mo  $K\alpha$  radiation. The diffraction pattern shows the typical features of the  $\text{Cu}_2\text{MnAl}$  structure, the superlattice reflexions (111) and (200) are present. A differentiation between the  $\text{Cu}_2\text{MnAl}$  and the  $\text{LiMgPdSn}$  structure is not possible since the calculated XRD patterns of these two structures are almost identical.

86x111mm (600 x 600 DPI)