X-Ray Investigations of the Intermetallic Phases $CaCd_{1-x}Tl_x$ and $CaIn_{1-x}Tl_x$ and Knight Shift Measurements of ^{205}Tl- and ^{113}Cd-NMR in the System $CaCd_{1-x}Tl_x$

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The quasibinary systems $CaCd_{1-x}Tl_x$ and $CaIn_{1-x}Tl_x$ form continuous series of solid solutions for all concentrations x: $0 \leq x \leq 1$. All alloys of both systems crystallize with space group O_h^1-Pm3m and one formula unit per unit cell (CsCl-type structure). Considerable deviations from Vegard's law occur for $CaCd_{1-x}Tl_x$, while they are negligible for $CaIn_{1-x}Tl_x$. No sign for the appearance of superstructures was found in either system after equilibrating them at 300 °C for two hours. In the system $CaCd_{1-x}Tl_x$ the Knight shift K_s of the ^{205}Tl- and ^{113}Cd-NMR was measured at room temperature as a function of x. Saturated $Tl(CH_3CO_2)$- and $Cd(NO_3)_2$ solutions served as reference samples. The Knight shift of the ^{205}Tl-resonance increases remarkably with increasing concentration x, whereas the Knight shift of the ^{113}Cd-NMR decreases slightly with increasing x. No simple qualitative explanation is found for $K_s(Tl) = f(x)$ and $K_s(Cd) = f(x)$.

Introduction

Recently, a number of X-ray investigations have been performed on ternary intermetallic phases of the composition Li_2XY (X = Cu, Ag, Au, and Mg; Y = Al, Ga, In, Tl, Si, Ge, Sn, Pb, Sb, and Bi) and of the composition $AgMg_{1-x}Y_x$ (Y = Ga, In, and Sn)[1−4]. The Li_2XY alloys crystallize with cubic face centered structures, which are related to either the NaTl-type or the $L2_1$-type (Heusler-phase). The second group, $AgMg_{1-x}Y_x$, shows basically the B2-type structure with further ordering towards the $L2_1$-type structure of the Heusler phase. Phase width and physical properties such as colour or electronic transport coefficients [5] depend strongly on the valence electron concentration (VEC).

Basically, the crystal structures of all the intermetallic systems mentioned above can be considered as superstructures of the primitive CsCl-lattice (B2-type). It therefore seemed to be of interest to investigate a simple quasibinary system

$$AB_{1-x}C_x (0 \leq x \leq 1),$$

with CsCl structure and a reasonable variability of the VEC with varying composition x. Another supposition was the intrinsic possibility to study concentration dependent nuclear magnetic resonance shifts (NMR-shifts, Knight shifts). The system $CaCd_{1-x}Tl_x (0 \leq x \leq 1)$ was chosen suitable for

such experiments. The binary alloys CaTl and CaCd crystallize both with the CsCl structure. In case of a complete solid solution, $0 \leq x \leq 1$, the VEC changes linearly with the concentration x within the limits $2.0 (x=0)$ VEC $2.5 (x=1)$. Furthermore, the nuclei ^{111}Cd, ^{113}Cd, ^{203}Tl, and ^{205}Tl are rather easy to access by NMR experiments.

Experimental

a) Preparation of the Alloys

The alloys were prepared from the elements, using metals of the following purities: Ca (98.5%), Merck, Darmstadt; Tl (99.9%), Schuchardt, München; Cd (99.95%), and In (99.99%), Preussag, Hannover. Since the metals Ca and Tl and the alloys $CaCd_{1-x}Tl_x$ and $CaIn_{1-x}Tl_x$ are quite sensitive to moist air, the materials were handled in a glove box under dried CO_2. The elements were weighed and filled into iron crucibles within the glove box. The closed crucibles were removed from the glove box, filled with argon and sealed gastight by welding. The alloys were prepared tat temperatures of about 1100 °C. Homogenisation was achieved by shaking the molten alloys several times. The iron crucibles with the enclosed alloys were cooled to room temperature on air. Opening of the crucibles and filing of the alloys in order to prepare the samples for the X-ray powder diagrams as well as for the NMR experiments was done within the glove box. The alloys $CaIn_{1-x}Tl_x$ were prepared using the same procedure.

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A detailed description of the preparation procedure is given in [6].

b) Chemical Analysis

Eleven alloys within the series $CaCd_{1-x}Tl_x$ were prepared and analysed chemically. For the chemical analysis, the alloys were dissolved in diluted HNO_3. Calcium and Cadmium were determined by complexometric titration [7]. The chemical analysis of the Thallium content of the alloys was based on bromatometric determination of Tl [8]. The mean errors in the chemical analysis are: Ca $(\pm 0.1\%)$, Cd $(\pm 1\%)$, Tl $(\pm 0.2\%)$. In Table 1, the results of the chemical

Table 1. Results of the chemical analysis for the alloys $CaCd_{1-x}Tl_x$ used in this work.

Nr.	x	Ideal Composition of the Alloy	Composition According to the Chemical Analysis
1	0.0	$CaCd_{1.00}$	$Ca_{1.04}Cd_{0.96}$
2	0.2	$CaCd_{0.80}Tl_{0.20}$	$Ca_{1.03}Cd_{0.78}Tl_{0.19}$
3	0.3	$CaCd_{0.70}Tl_{0.30}$	$Ca_{1.02}Cd_{0.68}Tl_{0.29}$
4	0.40	$CaCd_{0.60}Tl_{0.40}$	$Ca_{1.03}Cd_{0.58}Tl_{0.39}$
5	0.45	$CaCd_{0.55}Tl_{0.45}$	$Ca_{1.03}Cd_{0.53}Tl_{0.44}$
6	0.50	$CaCd_{0.50}Tl_{0.50}$	$Ca_{1.02}Cd_{0.49}Tl_{0.49}$
7	0.50	$CaCd_{0.50}Tl_{0.50}$	$Ca_{1.03}Cd_{0.49}Tl_{0.48}$
8	0.55	$CaCd_{0.45}Tl_{0.55}$	$Ca_{1.02}Cd_{0.43}Tl_{0.55}$
9	0.60	$CaCd_{0.40}Tl_{0.60}$	$Ca_{1.02}Cd_{0.40}Tl_{0.59}$
10	0.80	$CaCd_{0.20}Tl_{0.80}$	$Ca_{1.03}Cd_{0.21}Tl_{0.77}$
11	1.00	$CaTl_{1.00}$	$Ca_{1.01}Tl_{0.99}$

analysis of the alloys are given. No chemical analysis has been carried out for the alloys $CaIn_{1-x}Tl_x$.

c) X-ray Analysis

The filings for the X-ray powder-diffraction experiments were enclosed in capillaries of Lindemann-glass $(\varnothing = 0.3\,\mathrm{mm})$ within the glove box and annealed at 300 °C for two hours. The X-ray analysis was performed by the Debye-Scherrer-Straumanis method using Cu-Kα radiation and a camera with a radius of $180/\pi$ mm. The lattice constants were determined by the Nelson-Riley extrapolation method [9].

d) NMR Spectra

The filings for the NMR measurements were sieved, and only particles with a mean diameter $d \leq 0.04$ mm were collected for the experiments. These samples were annealed at 300 °C for two hours. The filings were suspended in paraffin oil to minimize the skin effect. The NMR measurements were done at room temperature using a Varian wide line spectrometer Type 4200 B. The frequency of the oscillator was locked to a quartz stabilized oscillator and the NMR spectrum was recorded by sweeping the magnetic field. Saturated aqueous solutions of $Cd(NO_3)_2$ and of $Tl(CH_3COO)$ served as reference samples. The NMR resonance lines of ^{205}Tl and of ^{113}Cd have been used for the determination of the Knight shifts. The fixed frequencies were 15,600 MHz for the ^{205}Tl and 15,400 MHz for the ^{113}Cd resonance, respectively. Since the ^{205}Tl resonances are fairly strong, a simultaneous recording of the resonance frequency of ^{205}Tl in the alloys $CaCd_{1-x}Tl_x$ and the solution of $Tl(CH_3COO)$ was possible. The ^{113}Cd resonances of the alloys were recorded separately in successive runs for the alloys and the standard.

Results

The X-ray investigation of the quasibinary system $CaCd_{1-x}Tl_x$ shows that a complete series of solid solutions exists for $0 \leq x \leq 1$. The alloys crystallize with space group O_h^1-Pm3m and one formula unit within the unit cell. No ordering at the point position of $(Tl + Cd)$ was observed over the whole range of x. In Figure 1, the lattice constants of $CaCd_{1-x}Tl_x$ are shown graphically as a function of x. An appreciable deviation from Vegard's law occurs. In Table 2, the results of the lattice constant determination are given. For the quasibinary system
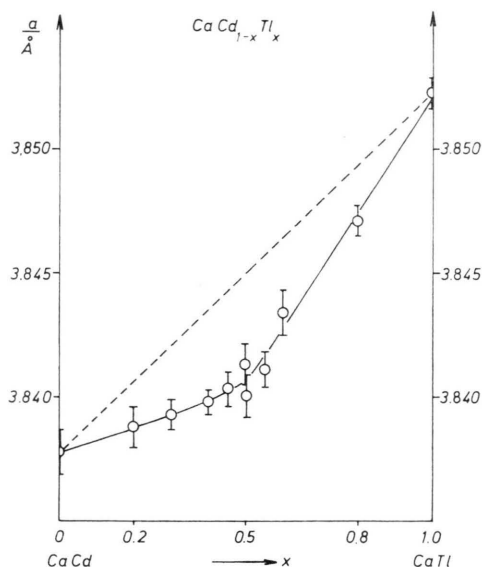

Fig. 1. Lattice constants a in the system $CaCd_{1-x}Tl_x$ as a function of x.

Table 2. Lattice constants of the alloys $CaCd_{1-x}Tl_x$ and $CaIn_{1-x}Tl_x$.

a) $CaCd_{1-x}Tl_x$

x	At-% Ca	Cd	Tl	Lattice Constant a Å
0	50	50	0	3.8378 ± 0.0009 I
0.2	50	40	10	3.8388 ± 0.0008
0.3	50	35	15	3.8393 ± 0.0006
0.4	50	30	20	3.8398 ± 0.0005
0.45	50	27.5	22.5	3.8403 ± 0.0007
0.5	50	25	25	3.8403 ± 0.0009 II
0.5	50	25	25	3.8413 ± 0.0008 III
0.55	50	22.5	27.5	3.8411 ± 0.0007
0.6	50	20	30	3.8434 ± 0.0009
0.8	50	10	40	3.8471 ± 0.0006
1.0	50	0	50	3.8522 ± 0.0006 IV

I $a = 3.838$ Å [10]; II Sample a); III Sample b); IV $a = 3.855 \pm 0.004$ Å [11].

b) $CaIn_{1-x}Tl_x$

x	At-% Ca	In	Tl	Lattice Constant Å
0	50	50	0	3.8491 ± 0.0008 I
0.2	50	40	10	3.8495 ± 0.0012
0.5	50	25	25	3.8504 ± 0.0012
0.8	50	10	40	3.8518 ± 0.0008
1.0	50	0	50	3.8522 ± 0.0006

I $a = 3.856 \pm 0.002$ Å [12].

$CaIn_{1-x}Tl_x$, the existence of solid solutions with CsCl-type structures (space group: O_h^1-Pm3m, $Z = 1$) could be established for all concentrations x. A superstructure due to an ordering of the In- and Tl-atoms was not observed. The results for this series are shown in Fig. 2 and Table 2. In contrast to
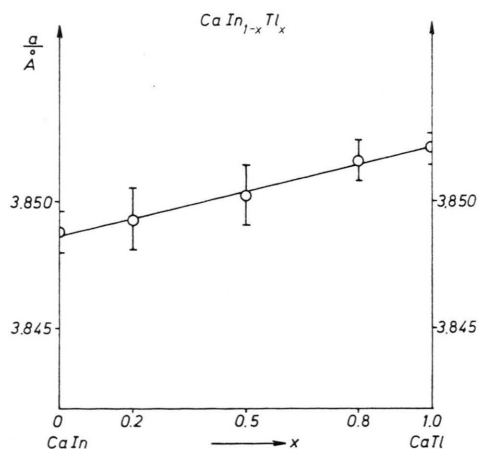
Fig. 2. Lattice constants a in the system $CaIn_{1-x}Tl_x$ as a function of x.

the system $CaCd_{1-x}Tl_x$, the system $CaIn_{1-x}Tl_x$ shows only a negligible deviation from Vegard's law.

The Knight shift of the [205]Tl-NMR was measured in the system $CaCd_{1-x}Tl_x$ covering the concentration range $0.2 \leq x \leq 1$. As usual, the Knight shift is defined as the relative shift of the resonance field with respect to the resonance field of a reference sample

$$K_s = \frac{\Delta H}{H} = \frac{H_{reference} - H_{alloy}}{H_{reference}}.$$

The results found for the Knight shift of the [205]Tl resonance field are given in Table 3. The Knight

Table 3. Knight shift of the [113]Cd-NMR and the [205]Tl-NMR in the system $CaCd_{1-x}Tl_x$ (δH is the line-width).

1. [205]Tl-NMR-Shift; $H_{reference} = 6349.2$ G, $\nu = 15.600$ MHz

x	At-% Ca	Cd	Tl	H_{alloy} Gauss	$\frac{\Delta H}{H} \cdot 10^2$	δH Gauss
0.2	50	40	10	6292.4	0.895 ± 0.011	16.0
0.3	50	35	15	6288.6	0.954 ± 0.011	17.4
0.4	50	30	20	6287.0	0.980 ± 0.011	19.7
0.45	50	27.5	22.5	6283.5	1.034 ± 0.011	21.4
0.5	50	25	25	6281.4	1.068 ± 0.011	22.3 I
0.55	50	22.5	27.5	6277.2	1.135 ± 0.013	25.9
0.60	50	20	30	6270.0	1.247 ± 0.014	27.2
0.80	50	10	40	6257.8	1.440 ± 0.011	19.7
1.0	50	0	50	6243.4	1.666 ± 0.011	15.4

I for both samples a) and b).

2. [113]Cd-NMR-Shift; $H_{reference} = 13306.7$ G, $\nu = 15.400$ MHz

x	At-% Ca	Cd	Tl	H_{alloy} Gauss	$\frac{\Delta H}{H} \cdot 10^2$	δH Gauss
0	50	50	0	16244.7	0.380 ± 0.003	10.0
0.2	50	40	10	16249.7	0.350 ± 0.003	13.0
0.4	50	30	20	16251.9	0.336 ± 0.003	12.0
0.5	50	25	25	16255.9	0.311 ± 0.003	10.5 II

II for both samples a) and b).

shift for the [113]Cd resonance was determined in the concentration range $0 \leq x \leq 0.5$. The results of the measurements are given in Table 3 as well. Figure 3 shows the shifts for both nuclei [205]Tl and [113]Cd.

Discussion

The lattice constants for the two binary systems $CaCd_{1-x}Tl_x$ and $CaIn_{1-x}Tl_x$ are shown in Figs. 1 and 2 as a function of the mole fraction x. The deviation from Vegard's law is negligible for the system $CaIn_{1-x}Tl_x$. However, for the system $CaCd_{1-x}Tl_x$,

considerable deviations from Vegard's law are observed. For the atomic radii of eight coordinated atoms the following values are found in the literature
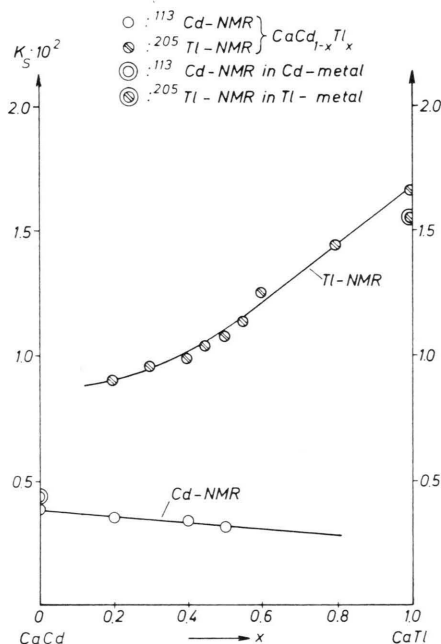

Fig. 3. Knight shift K_s of the ^{113}Cd-NMR and the ^{205}Tl-NMR in the alloys $CaCd_{1-x}Tl_x$ as a function of x. K_s of the ^{113}Cd-NMR in Cd metal [13] and K_s of the ^{205}Tl-NMR in Tl metal [14] are shown too.

(calculated according to Laves [15]): $r(Ca) = 1.911$ Å; $r(In) = 1.523$ Å; $r(Tl) = 1.659$ Å; $r(Cd) = 1.474$ Å. Assuming contact between next nearest neighbours in the binary alloys, the interatomic distances in the alloys are shorter than one expects from the atomic radii. The contractions of the interatomic distances in the alloys are: CaTl: 7%; CaIn: 3%; CaCd: 1.3%. This contraction of the atomic radius in the alloys is probably mainly due to a contraction of the Ca-atom. Thus, the deviation from Vegard's law within the series $CaCd_{1-x}Tl_x$ may be explained by a VEC dependent contraction of the atomic radius of the Ca-atom.

The Knight shift is a function of the product of the density of states at the Fermi energy and of the wave function density at the position of the nucleus considered. In a first qualitative approximation, the results of the Knight shift measurements can be interpreted with the free electron model. If we assume that the Ca-, the Cd-, and the Tl-atom contribute to the free electron concentration two, two, and three electrons, respectively, we expect the following behaviour of the Knight shift as a function of the Tl-concentration x: With increasing concentration x in the alloys $CaCd_{1-x}Tl_x$ the VEC increases and therefore an increase of the density of states can be expected, because the Fermi energy increases with increasing VEC and in the frame of the free electron model, the density of states increases with increasing energy.

With respect to the Knight shift of the ^{205}Tl resonance an increase of the shift parameter K_s with increasing x is proposed in accordance with the experiment (Fig. 3, Table 3). Also, the ^{113}Cd resonance shift should increase with increasing x in contrast to the experimental observation.

The NMR measurements in the system $CaCd_{1-x}Tl_x$ show that a qualitative interpretation of the experimental results is not very meaningful. It was, therefore, decided to compare the experiments with quantitative calculations, based on augmented plane wave calculations of the band structure of the alloys CaCd and CaTl. This work will be reported in a forthcoming paper.

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