Structural Investigation of ScAuSi and ScAuGe using ^{45}Sc Solid State NMR

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The hexagonal scandium compounds ScAuSi ($P\bar{6}m2$, a = 421.7(1), c = 680.7(1) pm) and ScAuGe ($P6_3mc$, a = 431.03(9), c = 685.5(1) pm) were synthesized in X-ray pure form *via* arc-melting of the elements. The structures are derived from the AlB_2-type. The gold and silicon (germanium) atoms build up strongly puckered layers of Au_3Si_3 and Au_3Ge_3 hexagons. Due to a different puckering pattern and stacking sequence of the hexagons, the ScAuGe structure has one and the ScAuSi structure two crystallographically independent scandium sites, which can be unambiguously distinguished on the basis of ^{45}Sc–^{29}Si magnetic dipole-dipole interactions measured in a site selective fashion on an isotopically enriched material by solid state NMR.

Key words: Scandium, Intermetallics, Crystal Chemistry, Solid State NMR

Introduction

Among the rare earth metals, scandium is by far the element with the smallest atomic size. This has clear consequences on the crystal chemistry of intermetallic scandium compounds. In many cases, scandium forms intermetallic compounds that are isotypic with the corresponding lutetium compounds, while in other cases, scandium is too small to realize such an atomic arrangement and consequently forms another, often new structure type. The crystal chemical and phase analytical data of the scandium intermetallics are summarized in two reviews [1, 2].

In the large family of $RE_xT_yX_z$ intermetallics (RE = rare earth metal; T = late transition metal; X = element of the 3rd, 4th, or 5th main group) the scandium atoms are sometimes slightly too small to form the structure of the corresponding lutetium representative. In such cases, however, slight structural distortions (superstructure formation) allow a very similar atomic arrangement. Recent examples for such superstructures are ScPtSn [3] and $Sc_3Rh_{1.594(9)}In_4$ [4].

Besides the X-ray crystallographic characterization of such superstructures, also ^{45}Sc solid state NMR is a useful technique for the determination of the different scandium sites in such intermetallics. In recent contributions we have reported on the first highly resolved ^{45}Sc spectra for the stannides ScAuSn [5], ScAgSn [6], and ScCuSn [7]. To explore the informational content of high-resolution ^{45}Sc NMR in intermetallic compounds in a broader context we have now started a more systematic investigation. Herein we report on the spectroscopic data of the known silicide ScAuSi [8] and the germanide ScAuGe [9, 10]. While the latter material contains one crystallographically independent scandium site only, the silicide has two crystallographically distinct Sc positions which differ significantly with respect to their Sc–Si and Sc–Au distances. In the present contribution we report a new ^{45}Sc{^{29}Si}rotational echo double resonance (REDOR) experiment, which serves to differentiate between the two crystallographically distinct sites on the basis of different heteronuclear dipolar interaction strengths.

Experimental Section

Synthesis

Starting materials for the preparation of ScAuSi and ScAuGe were scandium ingots (Kelpin), gold foil (Heraeus), silicon and germanium lumps (Wacker), all with stated purities better than 99.9 %. In a first step, small scandium pieces were arc-melted [11] to buttons under argon (600 mbar).

Table 1. ^{45}Sc chemical shifts (δ_{iso}) of ScAuSi and ScAuGe relative to 0.2 M scandium nitrate solution and MAS centerband linewidths (FWHH) Δ, are tabulated.

Compound	$\delta_{iso\,1}$ (ppm)	Δ (kHz)	$\delta_{iso\,2}$ (ppm)	Δ (kHz)
ScAuSi	720	2.3	1169	1.8
ScAuGe	976	3.2		

The argon was purified before over titanium sponge (900 K), silica gel and molecular sieves. The pre-melting procedure strongly reduces a shattering during the exothermic reactions with gold and silicon (germanium). The scandium buttons were then reacted with pieces of the gold foil and silicon (germanium) pieces in the ideal 1 : 1 : 1 atomic ratio in the arc-melting crucible. The resulting buttons were remelted three times to ensure homogeneity. The total weight losses after the arc-melting procedures were always smaller than 0.5 %. The arc-melted samples were polycrystalline. A sample of ScAuSi enriched with the ^{29}Si isotope (nominal enrichment level 90 %) was prepared in an analogous fashion for the ^{45}Sc{^{29}Si} REDOR experiments.

The bulk samples were analyzed by EDX using a LEICA 420 I scanning electron microscope with Sc, Au, SiO_2 and Ge as standards. The EDX analyses (33 ± 2 at.% Sc : 35 ± 2 at.% Au : 32 ± 2 at.% Si and 34 ± 2 at.% Sc : 34 ± 2 at.% Au : 32 ± 2 at.% Ge) revealed no impurity elements and was in agreement with the ideal 1 : 1 : 1 compositions.

X-Ray powder data

The purity of the samples was checked through Guinier powder patterns using Cu$K_{\alpha 1}$ radiation and α-quartz (a = 491.30, c = 540.46 pm) as an internal standard. The Guinier camera was equipped with an imaging plate system (Fujifilm BAS–1800). The hexagonal lattice parameters of a = 421.7(1), c = 680.7(1) pm for ScAuSi and a = 431.03(9), c = 685.5(1) pm for ScAuGe were obtained from least-squares fits to the Guinier data. To ensure proper indexing, the experimental patterns were compared to calculated ones [12] using the crystallographic data published previously [8, 10]. The present data are in good agreement with the lattice parameters reported earlier: a = 421.2(1), c = 680.3(2) pm for ScAuSi [8] and a = 430.82(5), c = 684.58(10) pm for ScAuGe [10].

^{45}Sc Solid state NMR spectroscopy

^{45}Sc MAS NMR spectra were recorded at ambient temperature at a resonance frequency of 97.2 MHz on a Bruker DSX-400 spectrometer, using 4 mm MAS NMR probes at a spinning frequency of 11 kHz. Typical measurement conditions were: pulse length 0.5 μs (22.5°, solid flip angle), recycle delay 0.5 s and 4000 scans. The ^{45}Sc chemical shifts are referenced to 0.2 M scandium nitrate aqueous solution. The ^{45}Sc{^{29}Si} REDOR studies were conducted on a 4 mm Bruker triple resonance probe, at a MAS frequency of 8 kHz, using the sequence of Schaefer and Gullion [13]. Commercial bandpass filters were used for both the ^{45}Sc and the ^{29}Si channels. The π-pulse lengths of ^{45}Sc and ^{29}Si were 5.5 – 6.0 μs and 8.0 – 9.0 μs, respectively. Phase cycling according to the XY4 scheme was used for the ^{29}Si pulses [14]. The number of scans was 12000 with a recycle delay of 2 s.

Results and Discussion

The structures of ScAuSi [8] and ScAuGe [9, 10] are displayed in Fig. 1. Both structures derive from the aristotype AlB_2 [15]. The gold and silicon (germanium) atoms build up layers of puckered Au_3Si_3 and Au_3Ge_3 hexagons. Within these layers, the Au–Si (249 pm) and Au–Ge (258 pm) distances are close to

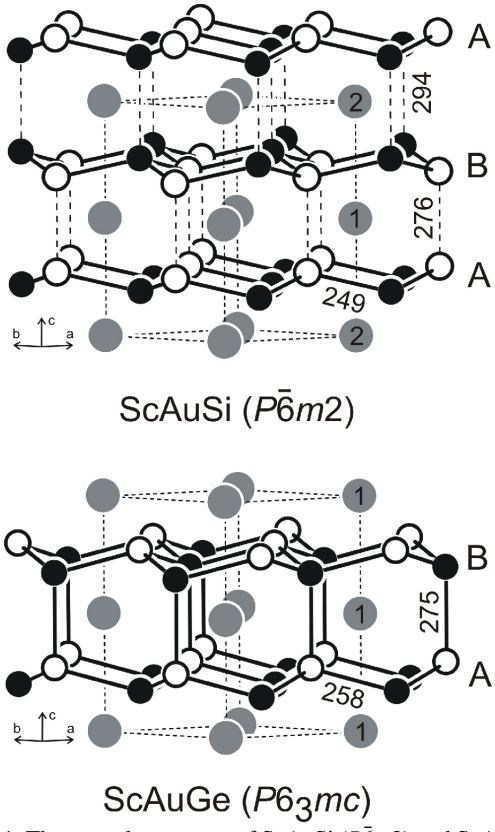

Fig. 1. The crystal structures of ScAuSi ($P\bar{6}m2$) and ScAuGe ($P6_3mc$). Scandium, gold, and silicon (germanium) atoms are drawn as medium grey, black filled, and open circles, respectively. The longer Au–Au and Si–Si contacts in ScAuSi are drawn with dotted lines. The crystallographically independent scandium sites and relevant interatomic distances (in pm) are indicated.

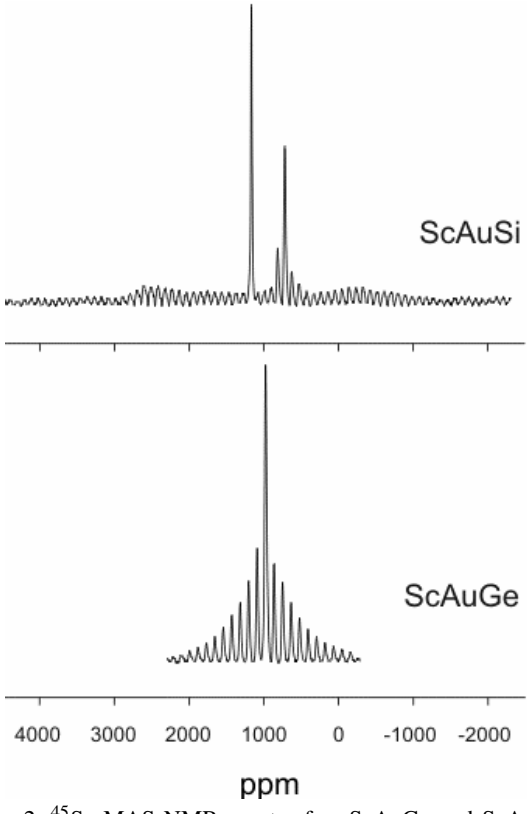

Fig. 2. ^{45}Sc MAS NMR spectra fror ScAuGe and ScAuSi measured at r. t. (spinning speed 11 kHz).

the sums of the covalent radii [12] of 251 (Au+Si) and 256 pm (Au+Ge), indicating covalent Au–Si and Au–Ge interactions within these layers.

The stacking sequence of the [AuSi] and [AuGe] layers is different in both compounds. In ScAuGe, every other layer is rotated by 60° around the *z* axis, and consequently each gold atom obtains a fourth germanium neighbor from the adjacent layer and *vice versa*. This way the gold atoms reach slightly distorted tetrahedral germanium coordination. The fourth neighbor at 275 pm has a slightly longer Au–Ge distance. The [AuGe] network is isopointal with the wurtzite structure and the scandium atoms fill trigonal prismatic voids in that substructure.

The situation is different for the ScAuSi structure. The [AuSi] layers are not rotated and the puckering of the network proceeds in a different manner. The gold and silicon atoms dislocate pairwise from the subcell mirror planes and move towards each other, leading to weak Au–Au (294 pm) and Si–Si (276 pm) contacts between the layers. Consequently the structure has two crystallographically independent scandium sites. The Sc1 atoms have six nearest silicon neighbors at a distance of 280 pm and six nearest gold atoms at a distance of 316 pm, while for the Sc2 atoms the situation is exactly the reverse one (Fig. 1).

Fig. 2 shows the ^{45}Sc MAS NMR spectra of both compounds. As expected, only a single resonance is observed for the germanide, while for the silicide the structural difference between Sc1 and Sc2 is clearly resolved by a 450 ppm resonance shift difference in the spectra. The low-frequency resonance shows significantly stronger signal broadening effects than the high-frequency resonance, which is attributable to the influence of second-order quadrupolar perturbations. As the two scandium sites differ substantially with respect to the Sc-Si distances they should be easily distinguishable by the magnitude of the ^{45}Sc-^{29}Si magnetic dipole-dipole coupling. Thus a ^{45}Sc{^{29}Si} rotational echo double resonance (REDOR) experiment was conducted on a ^{29}Si enriched sample. In REDOR, the intensity of a rotor-synchronized spin echo signal is compared with a (diminished) intensity that is obtained when the heteronuclear dipolar interaction is re-coupled by applying 180° pulses during the MAS rotor period [13]. In the present application, this experiment turned out to be seriously handicapped by the short spin-spin relaxation time of the ^{45}Sc nuclei, severely restricting the range of dipolar evolution times that could be applied. Fig. 3 shows a superposition of the rotor synchronized ^{45}Sc spin echo signal with the ^{45}Sc{^{29}Si} REDOR signal (dashed curve), using a dipolar evolution time of 1.25 milliseconds. Clearly the signal attenuation caused by the re-coupled dipolar interaction is much more pronounced for the 720 ppm signal than it is for the 1169 ppm signal. Based on this result we can conclude that the former resonance belongs to the Sc1 site that interacts more strongly with the ^{29}Si nuclei. The present work underlines the power of advanced ^{45}Sc solid state NMR methodology in the structural characterization of scandium based intermetallics.

Acknowledgements

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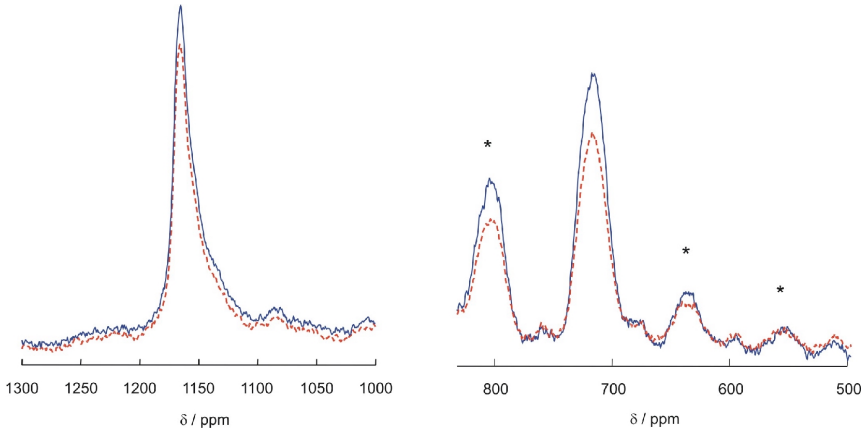

Fig. 3. ^{45}Sc{^{29}Si} MAS-NMR spectra of ScAuSi. Top curve: regular MAS spectrum obtained with a rotor-synchronized spin echo sequence. Bottom curve: spectrum obtained with ^{29}Si dephasing, using a dipolar evolution time of 1.25 ms, on a ^{29}Si enriched sample. Spinning side bands are marked with asterisks. The spectrum to the left shows the REDOR experiment on the 1169 ppm resonance (assigned to Sc2), the one to the right shows the REDOR experiment on the 720 ppm resonance (assigned to Sc1).

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