Crystal structure of calcium nickel digallide, $CaNiGa_2$

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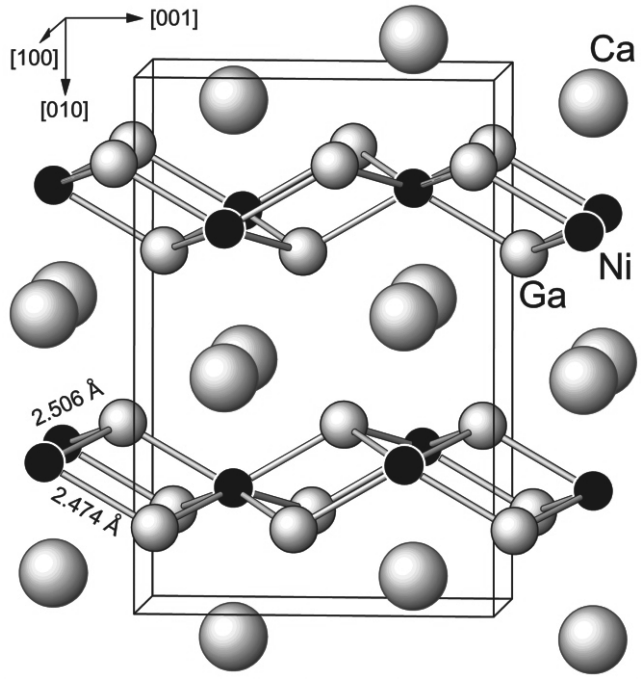

Abstract

$Ca_4Ga_8Ni_4$, orthorhombic, *Cmcm* (no. 63), a = 4.0578(1) Å, b = 10.3639(3) Å, c = 6.9592(2) Å, V = 292.7 Å^3, Z = 4, $R_{gt}(F)$ = 0.032, $wR_{ref}(F)$ = 0.028, T = 293 K.

Source of material

Starting materials for the preparation of $CaNiGa_2$ (total mass 1 g) were ingots of calcium (Alfa Aesar, 99.987 %), nickel foil (Lamprecht, 99.9 %) and gallium lumps (Chempur, 99.999 %). The elemental components were mixed in the stoichiometric ratio 1:1:2 and sealed into a tantalum tube under an argon pressure of about 800 mbar. The tantalum tube was subsequently enclosed in a quartz ampoule to prevent oxidation of tantalum at high temperatures. The following thermal treatment was carried out: heating to 1100 °C within 24 h, annealing at this temperature for 2 h, cooling to 600 °C with the rate 5 °C/h and subsequent annealing at this temperature for 60 days and quenching in cold water. Platelet-shaped single crystals were mechanically extracted from the annealed sample.

Experimental details

Lattice parameters were obtained by least-squares refinement using 51 reflections extracted from X-ray powder Guinier data (CuKα_1 radiation, λ = 1.54060 Å and LaB_6 with a = 4.15695 Å as internal standard).

Discussion

The title compound adopts the $MgCuAl_2$-type crystal structure [1,2], a ternary variety of Re_3B type [3,4]. In the crystallographic description of $CaNiGa_2$, calcium and gallium atoms are arranged in an ordered manner on the rhenium sites of Re_3B (4*c* and 8*f* sites, respectively). The location of Ni atoms (at 4*c* site) corresponds to those of boron in the parent structure. From the chemical point of view it is better to describe the title compound as $MgCuAl_2$ derivate with Ca, Ni and Ga atoms in the Mg, Cu and Al positions, respectively. Ni and Ga atoms are interlinked into a 2D polyanion. Each Ni atom is six-fold coordinated by Ga with Ni—Ga distances of 2.474 Å (2×) and 2.506 Å (4×). Comparing these values with the sum of the single-bond radii of 2.399 Å (r(Ni) = 1.154 Å, r(Ga) = 1.245 Å [5]), one can assume a considerable covalent interaction between these atoms with bond order of 0.80 and 0.70, respectively. Besides three Ni neighbors, each Ga has three further Ga atoms in its coordination sphere, which are located at significantly larger distances of 2.688 Å (1×) and 2.857 Å (2×). The wave-like $[NiGa_2]$ polyanionic slabs are stacked perpendicular to [010] and separated by Ca cations. The coordination sphere of Ca is formed by 3 Ni, 10 Ga and 2 further Ca atoms. The corresponding distances are 2.864 Å (1×) and 3.080 Å (2×) for Ca—Ni, 3.133 Å (4×), 3.211 Å (2×) and 3.326 Å (4×) for Ca—Ga, 3.681 Å (2×) for Ca—Ca contacts, respectively.

$CaNiGa_2$ is a Pauli paramagnet with χ = +41 × 10^{-6} emu/mol. Assuming a free electron model, the electronic density of states at the Fermi level yields 2.1 states/eV per formula unit.

Table 1. Data collection and handling.

Crystal:	grey platelet, size 0.020 × 0.050 × 0.070 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	268.9 cm^{-1}
Diffractometer, scan mode:	Rigaku AFC7, ω/φ
$2\theta_{max}$:	68.2°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	1350, 232
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 212
$N(param)_{refined}$:	11
Program:	WinCSD [6]

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Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ca	4*c*	0	0.4421(2)	¾	0.0159(6)	0.0117(6)	0.0127(6)	0	0	0
Ni	4*c*	0	0.2814(1)	¼	0.0118(4)	0.0120(4)	0.0132(5)	0	0	0
Ga	8*f*	0	0.16080(8)	0.5568(1)	0.0128(3)	0.0195(3)	0.0121(4)	0	0	–0.0000(2)

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