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$EuAl_2Ge$, its synthesis and property characterizations

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$EuAl_2Ge$, orthorhombic system, space group *Pnma* (No. 62), unit cell parameters: *a* = 7.294(2) Å, *b* = 4.306(1) Å, *c* = 11.237(4) Å, *V* = 352.9(3) Å^3, Mr = 1114.04, Dx = 5.2425(1) g cm^{-3}, F(000) = 484, Z = 4, μ = 1262.5 cm^{-1} (Cu Kα1, 1.54056 Å), *ab initio* structure model with full profile refinement from a powder pattern (211 reflections and 17300 profile points) for 14 free parameters resulted in R_I = 0.071, R_p = 0.152 and R_{DBWS} = 0.116 with goodness of fit = 0.580. The structure is related to the β-$YbAgGa_2$, $ScRhSi_2$ and YZn_3 types and can be considered as an intergrowth of $BaAl_4$- and distorted CaF_2-type columns. The magnetic susceptibility is characteristic of pure Eu^{2+} with μ_{eff} = 8.07 μ_B and antiferromagnetic ordering at ca. 25 K.

$EuAl_2Ge$ / Synthesis / Crystal structure / Rare earth / Powder diffraction

Introduction

In contrast to the pure trivalent rare earths, europium and ytterbium have in many cases shown to be stable as divalent cations or as mixed valence cations. In our systematic studies of ternary systems of Eu and Yb with main group elements, it was noted that two ternary compounds had previously been characterized in the Eu-Al-Ge system [1-3], and several new compounds have been characterized now [4]. Here we report a new compound, $EuAl_2Ge$ with a new structure type, its structure and property characterizations.

Experimental

Syntheses:
The as-cast samples of $EuAl_2Ge$ were synthesized by high frequency (HF) induction melting of pure metals (Eu 99.9%, Al 99.999%, Ge 99.9999%) in graphite crucibles inside an Ar glovebox. Europium was distilled prior to weighing. The detailed sample preparation and annealing procedure is similar to that used for $Yb(Al,Ge)_3$ compounds [5]. The samples have been annealed at 800ºC for 100 h prior to the final homogenization at 600ºC for 10 d and quenched in cold water. The annealed samples have normally not attacked the Mo foils.

Structure characterization:
In order to prevent severe decomposition of the samples in air and moisture the powder samples used for X-ray diffraction were all prepared inside an Ar glovebox with protection tape. Lattice parameter refinements were done from powder data using Si as an internal standard (λ = 1.54056 Å, *a* = 5.4305 Å). The data collection was carried out with a Huber670 camera system. The structures were solved by *ab initio* powder methods and refined from full profile powder XRD data by using CSD programs [6]. Full profile refinements (211 reflections and 17300 profile points) for 14 free parameters, including atom positional and isotropic displacement parameters, led to the residual values R_I = 0.0714 and R_p = 0.1524. The corresponding R_{DBWS} = 0.116. Since the absorption corrections were only carried out in an empirical manner, the refined values of the thermal parameters, which are strongly correlated to the absorption correction, represent only a rough estimation of the atomic displacements. The observed-calculated powder patterns together with their difference plot are shown in Fig. 1. The refined crystallographic results are listed in Table 1, atomic positional and displacement parameters in Table 2, interatomic distances in Table 3.

Property characterizations:
The magnetic properties were measured using a SQUID magnetometer (MPMS-XL7, Quantum Design), and electrical conductivity by a conventional four-probe-dc method.

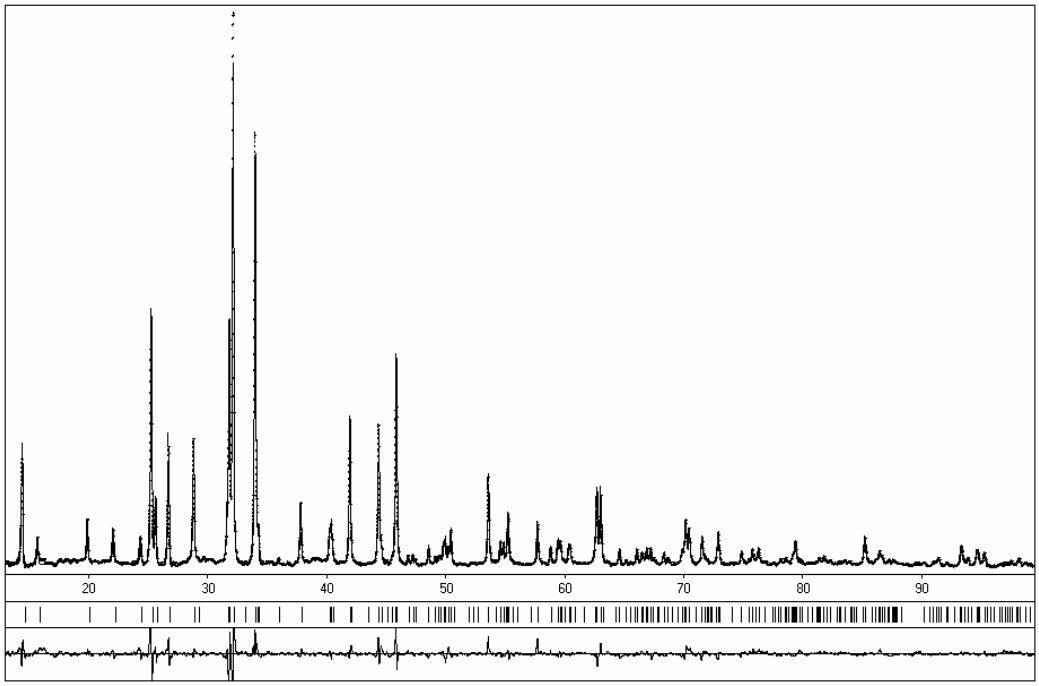

Fig. 1 The observed-calculated powder patterns together with the difference plot.

Table 1 Crystallographic data for $EuAl_2Ge$.

Crystal system	Orthorhombic
Structure type	New
Space group	*Pnma* (No. 62)
a (Å)	7.294(2)
b (Å)	4.306(1)
c (Å)	11.237(4)
V (Å^3)	352.9(3)
F(000)	484
Z	4
Dx (g cm^{-3})	5.2425(1)
μ (cm^{-1})	1262.5
Radiation, λ (Å)	Cu, 1.54056
Diffractometer	Powder
Mode of refinement	Full profile
No. of parameters	14
2θ (°), sinθ/λ max (Å^{-1})	99.57, 0.496
R_I, R_p, R_{DBWS}	0.0714, 0.1524, 0.116
Goodness of fit	0.580
Preferred orientation	[212], 1.4956

Results and discussion

Structure description:
Due to its high aluminium content, the compound can not be classified as a Zintl (or valence) compound. Fig. 2 shows an off [010] view of the structure. In the drawing, the bonded Al-Ge network is emphasized. It is clearly seen that the Eu atoms separate the Al-Ge network into well-confined infinite columns along the [010] direction. Each column is connected to four adjacent ones through Al-Ge exo-bonds. The aluminium atom arrangement inside the Al-Ge column, forming zigzag ladders along the [010] direction, can also be found in the $BaAl_4$ type structure [7]. The Ge atoms are bonded to three aluminium atoms on each side of the chain and form a so-called "butterfly shaped polyanion" consisting of three Al and one Ge. The whole Al-Ge chain can be considered to resemble a fused butterfly anion, see Fig. 2. If we consider the zig-zag ladder as a 5-electron polyanion [8] and four-bonded Ge as Ge^0, the compound can be formulated as $Eu^{2+}[Al^{2-}]_2Ge^0$, obviously not obeying the Zintl-Klemm electron counting rules. The Al-Ge and Al-Al interatomic distances, ranging from 2.464 Å to 2.717 Å and therefore falling in the single bond range, should not be saturated.

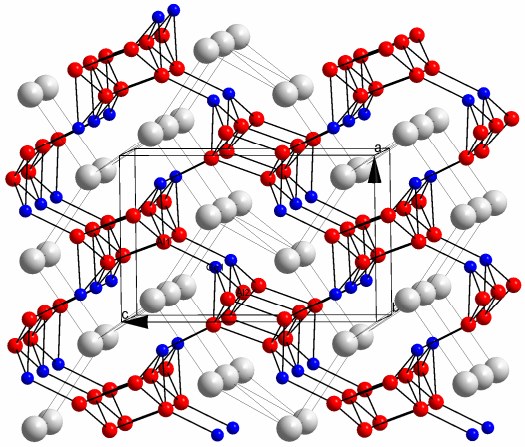

Fig. 2 Overview of the $EuAl_2Ge$ structure.

Table 2 Atomic positional and isotropic displacement parameters ($Å^2$) for $EuAl_2Ge$.

Atom	Site	*x*	*y*	*z*	U_{iso}
Eu1	4*c*	0.3600(1)	1/4	0.35988(9)	0.0109(3)
Al1	4*c*	0.9644(7)	1/4	0.6496(5)	0.033(2)
Al2	4*c*	0.3547(7)	1/4	0.0588(3)	0.011(1)
Ge1	4*c*	0.3188(2)	1/4	0.6423(2)	0.0093(6)

Table 3 Interatomic distances (Å) for $EuAl_2Ge$.

Eu1		
– 2Ge1 3.183(1)	– 2Al1 3.446(5)	– 2Al2 3.479(4)
– Ge1 3.190(3)	– Al2 3.388(4)	– 2Ge1 3.507(2)
– 2Al1 3.200(4)		
Al1		
– Al2 2.464(7)	– Ge1 2.584(5)	– 2Eu1 3.200(4)
– Ge1 2.571(6)	– 2Al2 2.717(4)	– 2Eu1 3.446(5)
Al2		
– Al1 2.464(7)	– 2Al1 2.717(4)	– 2Eu1 3.479(4)
– 2Ge1 2.673(3)	– Eu1 3.388(4)	
Ge1		
– Al1 2.571(6)	– 2Al2 2.673(3)	– 2Eu1 3.183(1)
– Al1 2.584(5)	– Eu1 3.190(3)	– 2Eu1 3.507(2)

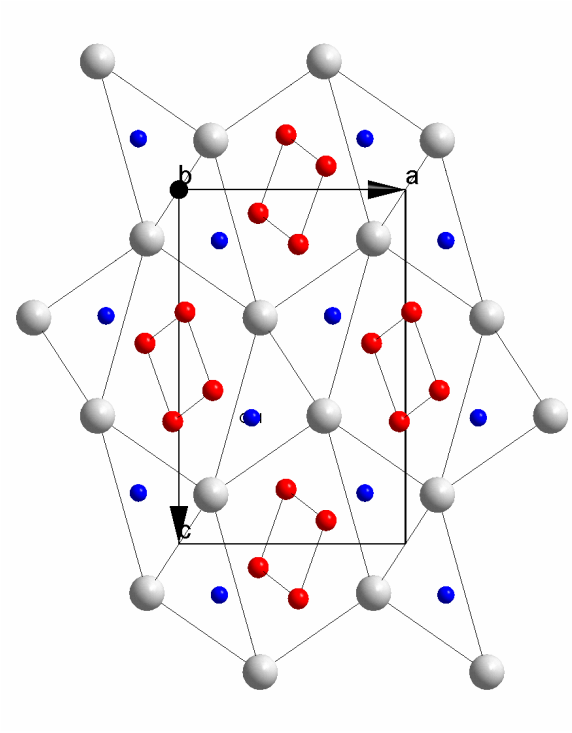

Fig. 3 Projection of the $EuAl_2Ge$ structure along [010] showing the intergrowth of $BaAl_4$-type and quite deformed CaF_2-type columns.

Geometrically, the Ge atoms are at centers of tri-capped trigonal prisms of 4Eu+2Al. The Al(1) atoms are also located at centers of tri-capped trigonal prisms of 4Eu+2Al. The Al(2) coordination is somewhat different from that of Al(1) and can be considered as a deformed square pyramid with 2Al+2Ge as basal plane and another Al as apex. The structure as a whole can be considered as an intergrowth of columns cut from both the $BaAl_4$ type and quite deformed CaF_2 type, as shown in Fig. 3.

The $EuAl_2Ge$ structure is closely related to the β-$YbAgGa_2$ structure [9] with the same space group and Wyckoff sequence. The ratios of the crystallographic axis are $a/b = 1.694$ and $c/b = 2.610$ for the former and 1.60 and 2.38 for the latter, respectively. Another related structure is the $ScRhSi_2$ type [10], which is isopointal to the gallide with similar ratios of 1.56 and 2.36, respectively. A comparison of the latter two types has been made by Grin et al. [9] and they were considered as ordered substitution variants of the YZn_3 type [11]. The current structure can also be considered as isopointal to the gallide and silicide structures if we do not take into account the exchange of sites occupied by main group elements and transition metals. The site exchange when Al or Ga participate in the structure is a not so rare feature among intermetallic compounds, see e.g. [12].

Physical properties:

The magnetic susceptibility in different external magnetic fields is shown in Fig. 4. The low-temperature details are magnified in the inset. The compound shows Curie-Weiss behaviour at high temperatures. By a direct fit of χ(T) in the range 70 K - 320 K to $C/(T_\theta)$ the magnetic moment is calculated to 8.07 μ_B, which is somewhat higher than expected for a pure Eu^{2+} compound (7.94 μ_B). The Curie-Weiss temperature θ is -3.8(1) K (afm).

At low temperatures a clear antiferromagnetic ordering is visible with a double transition at 26.0(3) K and 27.5(3) K. The Néel temperature T_N is

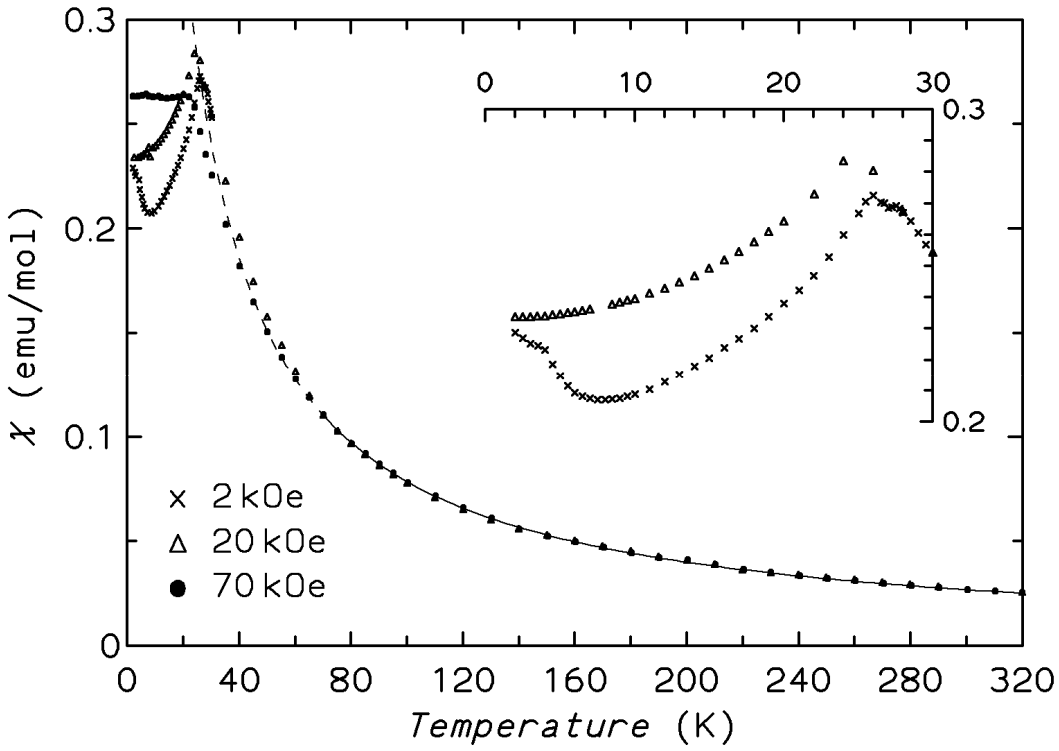

Fig. 4 Magnetic susceptibility of $EuAl_2Ge$ in different external magnetic fields. The fit to the 20 kOe data above 100 K is given.

quite large compared to the value of θ. T_N decreases with increasing external magnetic field, consistent with antiferromagnetic ordering of the Eu^{2+}. A small transition peak at 4.0(3) K – visible only in the 2 kOe field data – is preceeded by an increase of χ(T) towards lower temperatures, starting at 8.0 K. This could be interpreted as a re-ordering transition of the Eu^{2+} spins. The isothermal magnetization at 2.0 K increases still nearly linearly in an external field of 70 kOe and reaches only 3.3 μ_B in this field.

Acknowledgements
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