Refinement of the crystal structure of europium digallide, EuGa$_2$

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Abstract
EuGa$_2$, orthorhombic, Imma (no. 74), $a = 4.6459(3)$ Å, $b = 7.6255(5)$ Å, $c = 7.6379(3)$ Å, $V = 270.6$ Å$^3$, $Z = 4$, $R_{gl}(F) = 0.017$, $wR_{iet}(F) = 0.023$, $T = 293$ K.

Source of material
A series of samples with nominal compositions Eu$_{28-x}$Ga$_{72+x}$ (27 < $x$ < 40) was prepared by melting of elemental components in a high frequency furnace (open carbon crucible; argon atmosphere; europium, 99.9%, Lamprecht, additionally distilled; Ga, 99.9999%, Chempur). For homogenization, the samples were wrapped in Mo foil, sealed into argon filled (400 mbar) silica tubes, annealed for 500 h at 600 °C and finally quenched in cold water. Single crystals with metallic luster were extracted from the compact alloy with nominal composition Eu$_{33}$Ga$_{67}$.

Experimental details
The unit cell parameters were obtained from least-square refinement or 35 reflections taken from powder patterns (Guinier Huber G670 camera, CuK$_\alpha$ radiation, $\lambda = 1.54056$ Å) using germanium ($a = 5.657906$ Å) as internal standard.

Discussion
Europium digallide was initially found to have the hexagonal structure of the AIB$_2$ type [1,2]. Further investigations showed the orthorhombic structure of the KHg$_2$ type [3,4]. The phase with the crystal structure of the AIB$_2$ type was explained either to be a high-temperature modification [3] or to be stabilized by impurities [4]. The present investigation confirmed the orthorhombic crystal structure of the KHg$_2$ type reported earlier from X-ray powder data [3,4]. Our investigations showed that the phase with the KHg$_2$ atomic arrangement is formed only at stoichiometric ratio of the components (1:2). Slight deviations from the ideal composition (Eu$_{28-30}$Ga$_{72-70}$) lead to the formation of the phase with AIB$_2$ structure [5]. The four-bonded gallium atoms in the crystal structure of EuGa$_2$ form slightly puckered hexagonal nets with Ga—Ga distances of 2.653(1) Å and 2.6921(6) Å. The distance between the nets is slightly longer 2.811(1) Å. The europium atoms have coordination number 16 with 12 Ga and 4 Eu neighbors. The Eu—Ga distances cover a narrow range of 3.1474(6) Å - 3.4547(6) Å. Rare earth digallides adopt predominately the AIB$_2$ type of structure at ambient conditions [6]. Beside the reported phase, only TmGa$_2$ and LuGa$_2$ crystalize with KHg$_2$ type [7]. As unique representative of this series, YbGa$_2$ adopts the hexagonal CaIn$_2$ structure type at ambient conditions [1,8].

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$_{23}$ |
|------|------|----|----|-----|----------|----------|----------|----------|----------|----------|
| Eu   | 4e   | 0  | 16 | 0.04762(7) | 0.0070(3) | 0.0059(3) | 0        | 0        | 0        |
| Ga   | 8i   | 0  | 0.43435(1) | 0.66088(1) | 0.0066(4) | 0.0084(4) | 0        | 0        | -0.0005(3)|

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Crystal structure of dieuropium trigallium iridium, Eu$_2$Ga$_3$Ir

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Experimental details
Lattice parameters were obtained by least-squares fitting of 29 reflections extracted from X-ray powder diffraction Guinier data using CoK$_\alpha$ radiation (\(\lambda = 1.78896\,\text{	extmu}\text{m}\)) and LaB$_6$ as the internal standard (\(a = 4.15692\,\text{\textmu}\text{m}\)).

Discussion
The crystal structure of Eu$_2$Ga$_3$Ir adopts Mg$_2$Cu$_3$Si type [1] realizing an ordered variant of the hexagonal Laves phase MgZn$_2$ [2-4]. Europium atoms occupy positions of Mg species (4f), gallium and iridium are located in the 6h and 2a sites, respectively. The title compound is the first gallium representative reported with an ordered distribution of atoms on the zinc positions of the aristotype. The environment of each atom has the shape of a Frank-Kasper polyhedron with 16 (4 Eu + 3 Ir + 9 Ga), 12 (6 Ga + 6 Eu) and 12 (6 Eu + 2 Ir + 4 Ga) atoms in the coordination shells of Eu, Ir and Ga, respectively. The interatomic distances \(d(\text{Eu—Ir}) = 3.309(2)\,\text{\textmu}\text{m}, d(\text{Ga—Ir}) = 2.676(2)\,\text{\textmu}\text{m}\) and \(d(\text{Ga—Ga}) = 2.707(4)\,\text{\textmu}\text{m}\) are comparable with the sum of the respective atomic radii (\(r(\text{Eu}) = 1.984\,\text{\textmu}\text{m}, r(\text{Ir}) = 1.357\,\text{\textmu}\text{m}, r(\text{Ga}) = 1.351\,\text{\textmu}\text{m}\) [5]). On the other hand, Eu—Eu distances (3.4024(4) \(\text{\textmu}\text{m}\) and 3.436(2) \(\text{\textmu}\text{m}\)) are considerably shorter as usually observed in the intermetallic compounds with europium in the 4f$^7$ configuration (Eu$^{2+}$) [6,7].

Abstraction
Eu$_2$Ga$_3$Ir, hexagonal, P\text{\textit{6}}$_3$/\text{\textit{mmc}} (no. 194), \(a = 5.6785(2)\,\text{\textmu}\text{m}, c = 8.6911(5)\,\text{\textmu}\text{m}\), \(V = 242.7\,\text{\textmu}\text{m}^3\), \(Z = 2\), \(R_p(F) = 0.032\), \(wR_{\text{eq}}(F) = 0.028\), \(T = 293\,\text{K}\).

Source of material
Starting materials for the preparation (total sample mass 1 g) were ingots of europium (Hunan Institute of Rare Earth Metal Materials, 99.9\%), gallium lumps (Chempur, 99.999\%) and iridium foil (Lamprecht, 99.9\%). Europium was redistilled in vacuum before using. The elemental components were mixed in stoichiometric ratio and sealed into a tantalum tube under an argon pressure of about 800 mbar. The tantalum tube was subsequently closed in a silica ampule to prevent oxidation of tantalum at high temperatures. The synthesis was performed by slow heating of the reaction mixture to 900 °C, annealing for 48 h, lowering the temperature (2 K/h) to 600 °C, annealing for 2 weeks and quenching in cold water. A platelet-like single crystal was mechanically extracted from annealed sample with stoichiometric composition.

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Table 1. Data collection and handling.

| Crystal: | gray platelet, size 0.020 x 0.050 x 0.070 mm |
| Wavelength: | Mo Kα radiation (0.71073 Å) |
| μ: | 717.2 cm⁻¹ |
| Diffractometer, scan mode: | Rigaku AFC-7 & Mercury CCD, φ/ω |
| 2θααχ: | 67° |
| N(hkl)measured, N(hkl)unique: | 2129, 232 |
| Criterion for I(obs), N(hkl)p: | Iobs > 2 σ(Iobs), 212 |
| N(param)refined: | 11 |
| Programs: | WinCSD [12], ATOMS [13] |

Table 2. Atomic coordinates and displacement parameters (in Å²).

| Atom | Site | x   | y   | z   | U₁₁ | U₁₂ | U₁₃ | U₂₂ | U₂₃ | U₃₃ |
|------|------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Ir(1) | 2a   | 0   | 0   | 0   | 0.0084(4) | 0.0068(5) | 0.0094(4) | 0.0010(5) | 0.0068(6) | 0.0010(7) |
| Eu(1) | 4f   | ½   | ½   | 0.55235(1) | 0.0115(9) | 0.0068(6) | 0.0010(7) | 0.0068(6) | 0.0010(7) |
| Ga(1) | 6r   | 0.3178(5) | 0.1589(2) | ¼   | 0   | 0   | 0   | 0   | 0   |

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