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Bell-Like [Ga_5] Clusters in $Eu_3Li_{5+x}Ga_{5-x}$ (x = 0.15)

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Dedicated to Professor John D. Corbett on the occasion of his 85th birthday

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The new ternary gallide $Eu_3Li_{5+x}Ga_{5-x}$ was synthesized from its constituent elements that were heated at 900 °C and then subsequently annealed at 300 °C for 10 months. The crystal structure was established from single-crystal diffraction data. A new type of discrete gallium cluster was found in $Eu_3Li_{5+x}Ga_{5-x}$, namely a bell-like [Ga_5] unit with one single-, one four- and three three-bonded atoms. On the basis of its structural features, magnetic properties and calculated electronic density of states (DOS), the title compound is represented as $[Eu^{2+}]_3[Li^+]_5[(1b)Ga^{4-}]_1[(3b)Ga^{2-}]_3[(4b)Ga^{1-}]_1$ (xb = number of bonds, where x = 1–4). The new structural unit observed in this compound is compared with other [Ga_n] (n = 2–6) clusters found in binary gallium compounds.

Introduction

According to the definition given by Cotton[1] metal-atom clusters "*... contain a finite group of metal atoms which are held entirely, mainly, or at least to a significant extent, by bonds directly between the metal atoms even though some non-metal atoms may be associated intimately with the clusters.*" According to von Schnering[2], the metal-atom clusters can be seen as "*frozen-in redox steps between the element and its electron-saturated formal cation or anion*" that may appear as either polycationic or polyanionic units. In cationic form the clusters are built in the presence of strong electronegative elements, e.g. halogenides. Well known cationic clusters include $[Hg_2]^{2+}$ dumbbells in calomel[3] and $[Bi_9]^{5+}$ capped tetragonal antiprisms in $Bi_{12}Cl_{14}$.[4] In intermetallic compounds, where the difference between the electronegativities of the constituent elements is small, the clusters preferentially represent the anionic part of the structure.[2] The diversity of polyanionic clusters formed by metal elements of group 13 is widely represented in the works of Corbett.[5] Even though the icosahedral and icosahedral-based clusters are very common for these elements, the formation of larger homonuclear agglomerates is possible if suitable ligands separate the metal atoms. By applying a special synthesis technique Schnöckel et al. obtained a series of so-called metalloid clusters containing up to 77 aluminium or 84 gallium atoms.[6]

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The variations in the homonuclear gallium clusters present in alkali metal phases have been discussed and reviewed by Belin.[7] In Figure 1 we highlight the information known about the presence of gallium agglomerates in the crystal structures of MGa_n compounds where M is an alkali, alkaline-earth metal atom or europium. The type of agglomeration observed for the Ga clusters is related to the number of valence electrons per Ga atom (hereafter denoted as the valence electron concentration, VEC) and the size of the electropositive component.

Generally, the formation of anionic clusters is observed for alkali metal gallides with a Ga content of ca. 82–64%, which corresponds to VEC values of 3.14–3.56 e/Ga atom (cf. blue areas in Figure 1). It is remarkable that the anionic clusters in these compounds do not exist as discrete [Ga_n] units. The small agglomerates (in which the number of atoms in the homoatomic Ga clusters with a convex shape does not exceed 12) are interlinked through direct bonding, or through intermediate atoms or groups of atoms, to give three-dimensional frameworks with large cavities and channels that are occupied by the cations (e.g. $Li_9K_3Ga_{28.83}$[13]). The sole exception among the alkali gallides is Cs_8Ga_{11}[14] that has a VEC value of 3.73 e/Ga atom, and a structure that contains completely isolated pentacapped trigonal prismatic [Ga_{11}] units. The majority of phases containing discrete [Ga_n] clusters (red area in Figure 1) have VEC values of 4.66–5.28 e/Ga atom and are formed in the presence of large divalent cations (Sr^{2+}, Ba^{2+}, Eu^{2+}). To this group of phases we also ascribe MgGa that has a VEC of 5 e/Ga atom and a structure containing [Ga_4] tetrahedra separated by small Mg^{2+} cations, as well as Eu_3Ga_2 with a VEC value of 6 e/Ga atom and a structure containing isolated [Ga_2] dumbbells. In compounds with a VEC of 7 e/Ga atom and

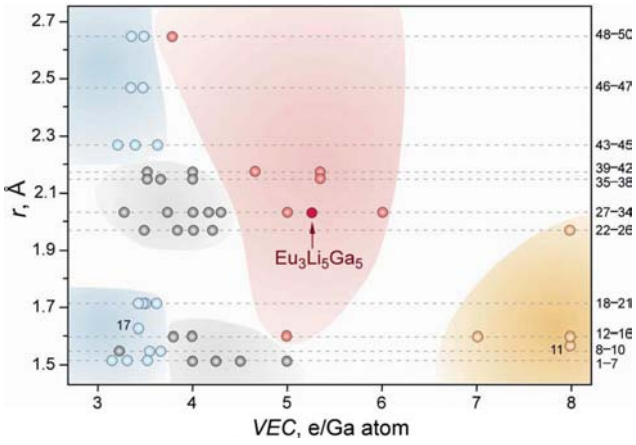

Figure 1. Cluster formation in the gallides MGa_n where M is an alkali, earth-alkali metal or europium, and its dependence on the VEC and the average atomic radius (r) of the M component(s).[8] The grey circles designate gallides in which clusters are not observed (instead chains, slabs, and 3D frameworks are present). The blue, red and orange circles correspond to compounds in which Ga atoms are present as interlinked [Ga_n] units, discrete [Ga_n] units, and as isolated atoms, respectively. The numbers on the right-hand side of the figure indicate phases containing atoms with the same atomic radii of the cation: 1 = Li_3Ga_{14}; 2 = $LiGa_{3.42}$; 3 = Li_5Ga_9; 4 = LiGa; 5 = Li_5Ga_4; 6 = Li_3Ga_2; 7 = Li_2Ga; 8 = $NaGa_4$; 9 = Na_7Ga_{13}; 10 = $Na_{22}Ga_{39}$; 11 = $LiMg_2Ga$; 12 = Mg_2Ga_5; 13 = $MgGa_2$; 14 = MgGa; 15 = Mg_2Ga; 16 = Mg_5Ga_2; 17 = $Rb_{0.6}Na_{6.25}Ga_{20.02}$; 18 = $K_4Na_{13}Ga_{49.57}$; 19 = $K_4Na_{13}Ga_{50}$; 20 = $K_4Na_{13}Ga_{47.45}$; 21 = $K_3Li_9Ga_{29}$; 22 = $CaGa_4$; 23 = $CaGa_{2.36}$; 24 = $CaGa_2$; 25 = Ca_3Ga_5; 26 = $Ca_{28}Ga_{11}$; 27 = $EuGa_4$; 28 = Eu_3Ga_8; 29 = $EuGa_2$; 30 = Eu_5Ga_9; 31 = Eu_3Ga_5; 32 = EuGa; 33 = $Eu_3Li_5Ga_5$; 34 = Eu_3Ga_2; 35 = $SrGa_4$; 36 = $Sr_{2.85}Ga_{8.45}$; 37 = $SrGa_2$; 38 = Sr_8Ga_7; 39 = $BaGa_4$; 40 = $BaGa_2$; 41 = Ba_5Ga_6; 42 = Ba_8Ga_7; 43 = K_3Ga_{13}; 44 = KGa_3; 45 = K_2Ga_3; 46 = $RbGa_7$; 47 = $RbGa_3$; 48 = $CsGa_7$; 49 = $CsGa_3$; 50 = Cs_8Ga_{11}. Crystallographic information is taken from ref.[9–12]

higher only isolated monoatomic Ga anions are observed (orange area in Figure 1). It follows from the facts discussed above that the isolated [Ga_n] clusters are formed over a relatively narrow interval of VEC values centered around 5 e/Ga atom for phases containing small cations. This VEC range is extended when the compound contains large cations. Besides adjusting the VEC value, the size and shape of the discrete anionic clusters could also be tuned by including a mixture of cations in the crystal structure to enhance its packing complexity.[15,16] In this paper we report an attempt to demonstrate the effectiveness of this approach for small gallium clusters.

Results and Discussion

An investigation of the Eu-Li-Ga system resulted in the synthesis of a $Eu_3Li_{5+x}Ga_{5-x}$ phase that contains a new type of discrete gallium cluster.[17] The bell-like [Ga_5] units (alternatively described as a tetrahedron with one pendant atom attached) in the structure of $Eu_3Li_{5+x}Ga_{5-x}$ are completely screened by the cations (Figure 2). The pear-shaped environment of each cluster is defined by 12 Eu and 13 Li atoms that constitute the triangular faces of four adjacent [Eu_6] octahedra and an ensemble of Li atoms that comprise a puckered Li_7 hexagon with an Li atom at the centre and three Li_2 dimers. The shortest Ga–Ga distance between the clusters, 4.685(1) Å, significantly exceeds the average value of 2.710 Å for the Ga–Ga bonds within the [Ga_5] units, indicating the absence of any direct interaction between the pentamer units within the structure. The [Ga_5] cluster is formed from one single-bonded [(1b)Ga1], one four-bonded [(4b)Ga3], and three three-bonded [(3b)Ga2] gallium species. As expected, the shortest bond within the [Ga_5] unit involves the single-bonded atom: d(Ga1–Ga3) = 2.486(3) Å; the remaining six bonds are considerably longer: d(Ga3–Ga2) = 2.692(2) Å (3×) and d(Ga2–Ga2) = 2.800(1) Å (3×). The bonding situation within the [Ga_5] cluster resembles that found in the α-modification of gallium,[18] in which short Ga–Ga dimers (d = 2.465 Å) interconnect corrugated hexagonal close packed layers [d(Ga–Ga) = 2.700–2.792 Å]. While the nonconvex shape of the bell-like [Ga_5] unit is quite unusual for clusters in intermetallic compounds, examples of gallium agglomerates with nonconvex shapes and small values of n can be found for metalloid [Ga_n] clusters.[6] The eight gallium atoms in $Ga_8[C(SiMe_3)_3]_6$ are arranged at the apices of two tetrahedra that are connected by a Ga–Ga bond.[19] The [Ga_5] unit reported herein could be considered as a substructure of this metalloid [Ga_8] cluster. The formation of more complex forms of metalloid clusters than those observed for $Ga_8[C(SiMe_3)_3]_6$ could be explained by increased screening of the [Ga_n] units by organic ligands.

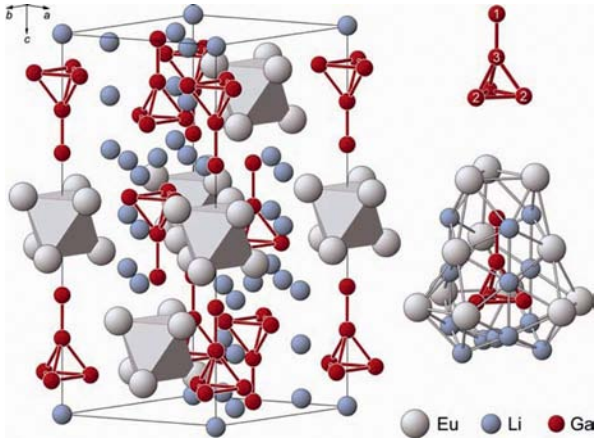

Figure 2. Crystal structure of $Eu_3Li_5Ga_5$ represented as an arrangement of [Eu_6] octahedra and bell-like [Ga_5] clusters separated by lithium cations. On the right-hand side of the figure the [Ga_5] unit with enumerated atoms as well as the environment of the [Ga_5] cluster defined by neighbouring Eu and Li cations are shown.

Taking into account the presence of differently coordinated Ga species within the bell-like [Ga_5] cluster (one single-, one four- and three three-bonded atoms) as well as the results from magnetic susceptibility measurements,[20] the crystal structure of the title compound can be represented, according to the Zintl concept, as $[Eu^{2+}]_3[Li^+]_5[(1b)Ga^{4-}]_1[(3b)Ga^{2-}]_3[(4b)Ga^{1-}]_1$.

The electron counting results performed with the Zintl method are in good agreement with the calculated electronic DOS (Figure 3). A gap that is expected from the electron-balancing count is not obtained in the calculation results, but at the Fermi level (E_F) a distinct dip is observed that is clearly visible in the spin-down section of the plot. Below the Fermi level two large regions of DOS are observed. The low energy region ($E < -4$ eV) is formed mainly from the Ga(*s*) states, the region within the $-3\text{ eV} < E < E_F$ range is formed predominantly from the Ga(*p*) bands. The Ga states reflect the formation of the [Ga_5] anions. The Li and Eu(*s*) states contribute to the whole DOS below E_F in agreement with the Zintl bonding picture, Eu(*d*) and Eu(*f*) states are observed at $E > -3$ eV, and the Eu(*f*) states are clearly localized.

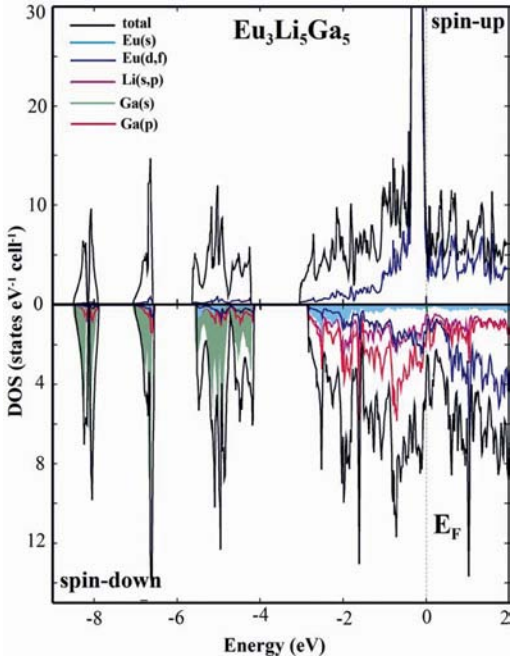

Figure 3. Electronic density of states for $Eu_3Li_5Ga_5$.

The electron counting results for the reported compound are also in good agreement with the issues associated with the formation of gallium clusters that were discussed in the introduction. With its VEC value of 5.33 e/Ga atom and a weighted average radius of the constituent cations of 2.04 Å, $Eu_3Li_5Ga_5$ is located in the expected region for compounds with discrete gallium clusters (cf. the red area in Figure 1). The tendency of gallium atoms to form homonuclear arrangements with different dimensionalities (chains, slabs, 3D networks) is well known, and numerous examples have been described for binary and ternary intermetallic phases.[21–24] In most of these networks the Ga–Ga distances vary within the range of 2.60–2.90 Å.[9] Nevertheless, in some structures it is possible to distinguish compact isolated agglomerates, [Ga_n]. The discrete [Ga_n] clusters, described up to now as being present in binary rare-earth and alkaline-earth gallides, normally do not contain a large number of atoms ($n \leq 6$, Figure 4). The simplest building units, isolated [Ga_2] dumbells, are observed in Eu_3Ga_2 (space group *C*2/*c*, own crystal structure type),[25] Th_3Ga_2 (space group *P*4/*mbm*, U_3Si_2 type of crystal structure)[26] and Gd_3Ga_2 (space group *I*4/*mcm*, own crystal structure type).[27] Surprisingly, the Ga–Ga distances vary greatly: 2.585 Å (Eu_3Ga_2), 2.654 Å (Th_3Ga_2) and 2.801 Å (Gd_3Ga_2). However, the interaction between the gallium atoms within the [Ga_2] units can be very different as shown, for example, by the phases with a 5:3 stoichiometry. Taking into account the Ga–Ga distance of 2.665 Å for the [Ga_2] dumbbells in the yttrium gallide Y_5Ga_3 (space group *P*4/*ncc*, Ba_5Si_3 type of crystal structure)[28] we assume that there is a significant direct interaction between the gallium atoms in this unit. The interatomic distances within the Ga pairs found in Sc_5Ga_3 (space group *C*2/*m*, own crystal structure type)[29] are 2.914 Å and 3.139 Å, which significantly exceed the sum of the atomic radii indicating weak Ga–Ga interactions and are rather suggestive of possible of multi-centre bonding.

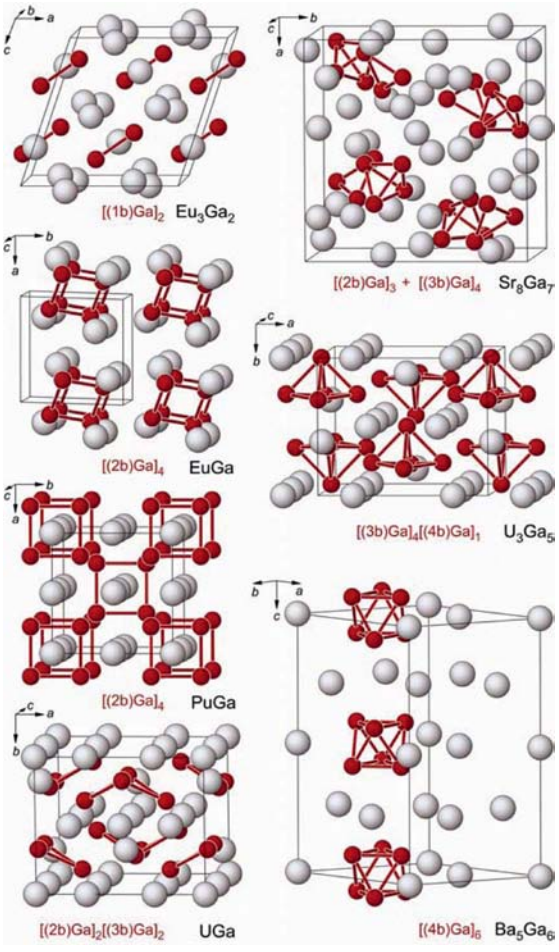

Figure 4. The [Ga_n] clusters (n = 2–6) in the binary gallides, MGa_n.

The crystal structure of Sr_8Ga_7 (space group $P2_13$, Sr_8Al_7 type of crystal structure)[30] consists of two different kinds of [Ga_n] cluster: triangles with *d*(Ga–Ga) = 2.673 Å and tetrahedra with Ga–Ga distances of 2.674 Å and 2.728 Å. It should be mentioned that all clusters in the

structure of Sr_8Ga_7 are completely separated by strontium atoms. The shortest distance between gallium atoms belonging to different agglomerates is 4.975 Å. Another example of a four-membered cluster is the planar rhombus found in the europium monogallide EuGa (space group $P\bar{1}$, own crystal structure type)[25] with d(Ga–Ga) = 2.625 Å and 2.647 Å and ∠Ga–Ga–Ga = 101.5°. An ideal square arrangement of gallium atoms is present in the tetragonal crystal structure of PuGa (space group $I4/mmm$, own crystal structure type)[31] with Ga–Ga distances of 2.749 Å. A butterfly-like cluster is observed in the structure of UGa (space group $Cmcm$, own crystal structure type)[32] that can be regarded as intermediate between a planar [Ga_4] unit and a tetrahedron. The two kinds of Ga–Ga interaction within this agglomerate are completely different. The shortest Ga–Ga distance of 2.487 Å is comparable with the shortest distance of 2.465 Å found in elemental gallium (α-Ga) indicating a strong interaction between the atoms comprising the body of the "butterfly"; the distance between the "alary" atoms are considerably longer [d(Ga–Ga) = 2.865 Å].

As an example of clusters with n = 5 we consider the tetragonal pyramids that are observed in the structure of U_3Ga_5 (space group $Cmcm$, Pu_3Pd_5-type of crystal structure).[33] The Ga–Ga distances within the base of the pyramid (2.704 Å) and between the atoms of the base and the apical atom (2.807 and 2.883 Å) are very close to those discussed above for the different [Ga_n] clusters. In the crystal structure of Ba_5Ga_6 (space group $P\bar{6}c2$, own crystal structure type)[34] the gallium atoms are condensed into octahedra with Ga–Ga distances of 2.713 and 2.747 Å. The octahedra are located in the hexagonal channels formed by the barium atoms. There are no contacts between the octahedra within the channels, and the shortest Ga–Ga distance between neighbouring octahedra is 3.836 Å (Figure 4). In general, there is no unique relationship between the Ga–Ga distances and the number of atoms in the [Ga_n] clusters for $2 \leq n \leq 6$ (Figure 5).

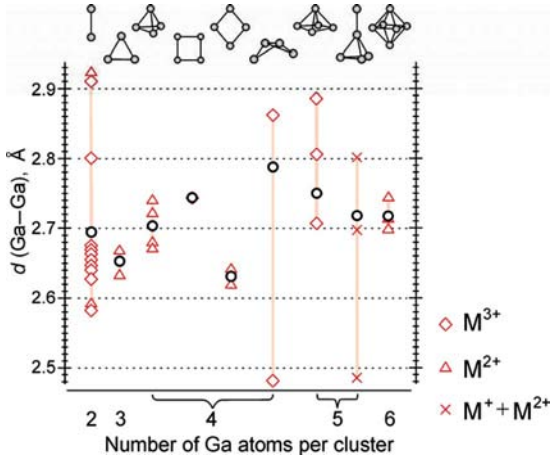

Figure 5. Interatomic distances observed in [Ga_n] clusters of different shapes.

Conclusions

The bell-like [Ga_5] unit found in $Eu_3Li_5Ga_5$ is the first five-membered nonconvex Ga cluster observed in an intermetallic phase. Its stabilization is provided by the presence of cations of different sizes in the crystal structure. Despite its unusual shape the [Ga_5] unit fits well into the general scheme that explains the dependence of gallium cluster agglomeration on the VEC.

Experimental Section

General: A set of samples with an approximate composition of $Eu_3Li_5Ga_5$ was prepared from elements of high purity: Li, 99.9 wt.-%, Alfa; Ga, 99.99 wt.-%, ChemPur; Eu, 99.9 wt.-%, Ames. Typically, a mixture of the starting components with a total mass of ca. 1.5 g was welded into a niobium tube that was placed in an evacuated and sealed quartz ampoule. The following heat treatment was performed: (i) heating to 900 °C at a rate of 40 °C/h; (ii) treatment at 900 °C for 2 h; (iii) cooling to 300 °C at a rate of 25 °C/h; (iv) annealing at 300 °C for 10 months, followed by quenching of the reaction with cold water. All manipulations with the starting materials were performed inside an argon-filled glove box [$p(O_2/H_2O) \leq 1$ ppm].

The samples were characterized by powder X-ray diffraction (Huber G670 Imaging Plate Guinier camera, Co-$K_{\alpha 1}$ radiation: λ = 1.78897 Å, Si as internal standard with a = 5.43102 Å). Crystal structure determination[17] was performed by a single crystal technique (irregularly shaped crystal mechanically extracted from the bulk sample and enclosed in a glass capillary, STOE IPDS diffraction system, monochromatized Ag-K_α X-ray radiation: λ = 0.56086 Å, numerical absorption correction, SIR92[35] and WinCSD programs[36] for structural solution and refinement).

The magnetization of the sample was measured in a SQUID magnetometer (MPMS XL-7, Quantum Design) for temperatures between 1.8 K and 400 K and with magnetic fields up to 7 Tesla.

Electronic structure calculations and bonding analysis were carried out for the ordered structure model with the composition $Eu_3Li_5Ga_5$ (Ga3 position completely occupied with gallium) with the TB-LMTO-ASA program package.[37] The Barth–Hedin exchange potential[38] was employed for the LDA calculations. The radial scalar relativistic Dirac equation was solved to obtain the partial wavefunctions. As the calculation within the atomic sphere approximation (ASA) includes corrections for the neglection of the interstitial regions and partial wavefunctions of higher order,[39] the addition of empty spheres to the calculation was not necessary. The following atomic radii were applied in the calculations: r(Eu) = 2.054 Å, r(Ga1) = 1.541 Å, r(Ga2) = 1.663 Å, r(Ga3) = 1.541 Å, r(Li1) = 1.619 Å, r(Li2) = 1.595 Å, and r(Li3) = 1.578 Å. A basis set containing Eu(6s,5d,4f), Ga(4s,4p) and Li(2s) orbitals was employed for a self-consistent calculation with Eu(6p), Ga(4d) and Li(2p,3d) functions being downfolded. A spin-polarized calculation was also performed.

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[17] Crystallographic data: space group $R\bar{3}m$ (no. 166), a = 9.4859(5) Å, c = 21.882(2) Å, V = 1705.2(3) Å^3, Z = 6, F(000) = 2129, ρ_{calc} = 4.848(1) g/cm^3, μ(Ag-K_α) = 14.55 mm^{-1}, crystal dimensions: 0.030 × 0.050 × 0.120 mm^3, 25 parameters, $R(F)$ = 0.025, $\Delta\rho_{min}/\Delta\rho_{max}$ = –2.71/1.28 e/Å^3. Collected data: 2θ up to 47.60°, 6632 measured reflections, 702 symmetry independent reflections, 584 observed reflections [$I > 2\sigma(I)$], R_{int} = 0.065, numerical absorption T_{min}/T_{max} = 0.389/0.631. Atomic coordinates for $Eu_3Li_{5+x}Ga_{5-x}$: Eu, 18(h) x 2x z, x = 0.46969(3), z = 0.09212(2); Ga1, 6(c) 0 0 z, z = 0.31326(9); Ga2, 18(h) x 2x z, x = 0.56829(7), z = 0.23209(5); Ga3, 6(c) 0 0 z, z = 0.1996(1), occupancy: 5.11(4)Ga + 0.89Li; Li1, 18(h) x 2x z, x = 0.5012(13), z = 0.3593(8); Li2, 3(a) 0 0 0; Li3, 9(d) 1/2 0 1/2. Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-423056.
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