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The C-Eu (Carbon-Europium) System

12.011 151.96

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No phase diagram is available for the Eu-C system, although some data are available on compounds that are formed in the Eu-C system. [58Spe] did not include Eu in their investigation of the crystal structure of RE-C compounds, but later investigators reported structure data for several Eu-C compounds. [70Lap] reported the preparation of a monocarbide which they designated EuC_{1-x}, where x represents the amount of C that is missing in the compound. They claimed a cubic NaCl-type structure and reported lattice parameters of 0.5145 ± 3 nm in the presence of excess metal and 0.5141 ± 1.1 nm in the presence of excess C. These lattice parameters (Table 1) appear to fit well with those of the cubic Fe_4N-type RE_3C structures.

After unsuccessful attempts to prepare Eu_3C, Eu_2C_3, and EuC_2 from the elements, [72Col] reacted >99.9% pure Eu with HCN and $(CN)_2$ at elevated temperatures and obtained the compounds Eu_2C_3, EuC_2, and EuN_xC_y. X-ray data were obtained with Fe-filtered CoK_α radiation using a 114.6 mm Debye-Scherrer camera. Eu_2C_3 was found to crystallize with the cubic Pu_2C_3-type structure, in good agreement with the structure of neighboring sesquicarbides. Their data for Eu_2C_3 are listed in Table 1.

Other investigators reported some lattice parameter data for EuC_2, but a complete structure analysis has not been reported. [68Fai] synthesized EuC_2 from the elements in sealed Mo bombs in an argon-filled C tube furnace. EuC_2 gave anomalous X-ray patterns, more complex than those of LaC_2, CeC_2, or NdC_2, but reproducible with four different samples. This pattern was indexed tentatively as a bct with a = 1.215 and c = 0.7290 nm, accounting for all but two low index lines. [64Geb] produced EuC_2 by two methods: (1) reduction of Eu_2O_3 (99.9% pure, weight?) with spectrographic grade C (graphite) placed in a graphite crucible; and (2) melting of 2-to-1 mol mixture of C and Eu in a stainless steel bomb in a resistance tube furnace. X-ray powder diffraction patterns of the product using CuK_α radiation in both a 114.59-mm powder camera and a Siemens diffractometer showed the bct CaC_2-type structure, along with a second phase with a different type of structure. The second phase could be obtained in larger quantities in samples containing a lower C-to-Eu ratio and heated to a somewhat lower temperature.

The low-angle lines of this impurity could be indexed on the basis of an orthorhombic cell with a = 0.876, b = 1.123, and c = 0.719 nm, but the high-angle lines were not indexed satisfactorily [66Geb].

[82Sak] synthesized EuC_2 by two methods: (1) 99% pure Eu and spectrographic grade C (graphite) were sealed under vacuum in a silica capsule and heated at 1000 °C for 30 h; and (2) 99.999% Eu_2O_3 was mixed with C (graphite), pelletized, and heated in Mo under a flow of argon at 1800 °C for 5 h. An excess of 5 at.% C (graphite) was used to remove all of the oxygen. Powder X-ray diffraction patterns were taken using Ni-filtered $CuK_{\alpha 1}$ radiation with an internal standard of Si. Phase transformation was examined by differential thermal analysis in the temperature range 27 to 727 °C. The dicarbides obtained by each method had bct CaC_2-type structure, but each contained a second phase that could not be removed

Table 1 Eu-C Crystal Structure and Lattice Parameter Data

Phase	Composition range, at.% C	Pearson symbol	Space group	Strukturbericht designation	Prototype	Lattice parameters, nm a	c	Density, g/cm³	Reference
(Eu)	0	*cI*2	*Im*3*m*	*A*2	W	0.45827	···	5.244	[86Gsc]
Eu_3C	~25 to ~33	*cF*5	*Fm*3*m*	$L1_1'$	Fe_4N	0.5145(3) (a)	···	7.646(a)	[70Lap]
						0.5141(3) (b)	···	7.722(b)	[70Lap]
Eu_2C_3	~60	*cI*40	$I\bar{4}3d$	$D5_c$	Pu_2C_3	0.8368	···	7.530	[72Col]
αEuC_2	66.7	*tI*6	*I*4/*mmm*	$C11_a$	CaC_2	0.4082(36)	0.6701(56)	5.236	[64Geb, 82Sak]
βEuC_2	66.7	*cF*12	*Fm*3*m*	*C*1	CaF_2	0.5961(1)	···	5.519	[68Mat]
EuC_6	85.7	*hP*14	$P6_3/mmc$	···	EuC_6	0.4314(3)	0.9745(8)	4.737	[75Gue, 80Elm]
(C)	100	*hP*4	$P6_3/mmc$	*A*9	C (graphite)	0.24612	0.67090	2.266	[Pearson2]

(a) Eu-rich. (b) C-rich.

by annealing. The lattice parameters for EuC_2 with the CaC_2-type structure are listed in Table 1.

[67Kri] attempted to measure the $\alpha \rightleftarrows \beta$ transformation temperature of EuC_2 in a sealed Ta bomb, but could not attribute the phenomena they observed at 355 °C to EuC_2, because their X-ray pattern showed predominant lines for Eu. However, [82Sak] reported that tetragonal EuC_2 transforms to an fcc form at 350 °C, which is close to the temperature where [67Kri] had observed a change. This is accepted as the transformation temperature of EuC_2, but it is considerably lower than those of other REC_2 compounds. βEuC_2 has fcc structure of the CaF_2 type. No melting temperature data were found. [67Kri] were not able to determine the EuC_2-C eutectic temperature by thermal analysis, due to the high vapor pressure of Eu over EuC_2. Because Eu exhibits variable valence tendencies, the properties and parameters of its compounds do not follow the systmatic variations encountered between other rare earth systems.

[75Gue] and [80Elm] studied intercalation of Eu metal in C (graphite). Using direct action of metal vapor on graphite in metal or glass tubes sealed under vacuum, they obtained a 25% yield of intercalation with Eu at 500 °C after 20 days. The core of their sample remained pure graphite. They reported that the first-stage compound, EuC_6, has a hexagonal unit cell with the space group $P6_3/mmc$. The reported lattice parameters are in Table 1.

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The C-Gd (Carbon-Gadolinium) System

12.011 157.25

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No phase diagram is available for the Gd-C system. [58Spe] reported that Gd forms a tri-rare-earth carbide with a range of solubility (see "The Carbon-Rare Earth Systems," in this issue). Their report included lattice spacings for the C-rich Gd_3C compound, which is ferromagnetic at room temperature. See Table 1 for structure details of this cubic Fe_4N-type form. [73Hub] prepared specimens of trigonal "Gd_2C" by arc melting 99.9 wt.% Gd and spectrographic quality C (graphite) together under a Zr-gettered inert gas atmosphere. After remelting several times, samples were crushed and X-ray powder data were obtained using a 114.59-mm camera and Ni-filtered CuK_α radiation. Some free Gd was detected in the samples, and on the basis of ultraviolet emission spec-