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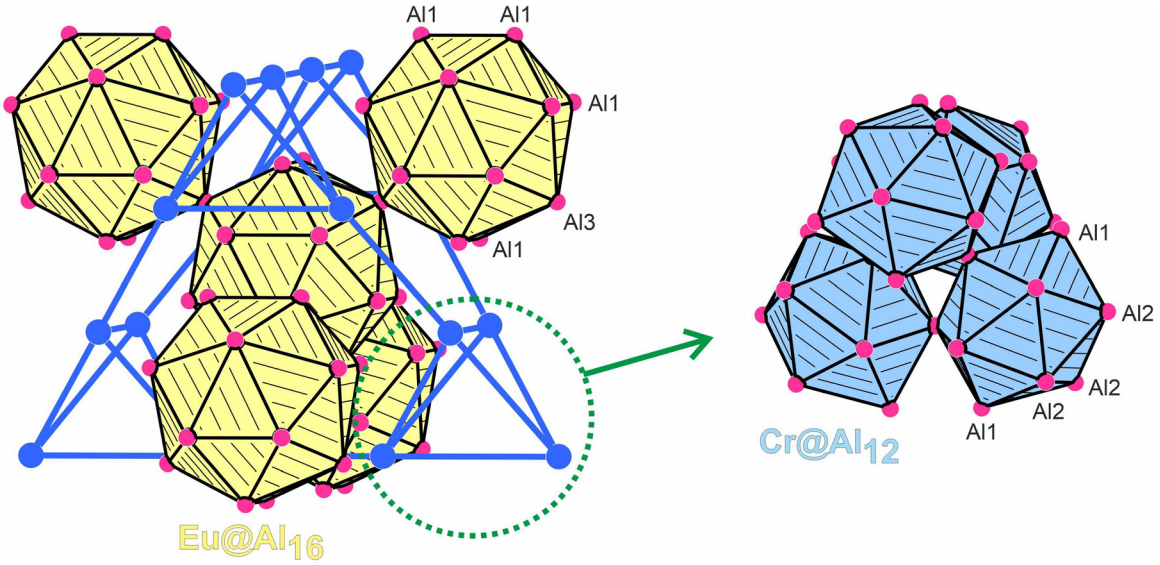
Crystal structure of europium dichromium icosaaluminum, $EuCr_2Al_{20}$



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Abstract

$EuCr_2Al_{20}$, cubic, $Fd\bar{3}m$ (no. 227), a = 14.5245(7) Å, V = 3064.1(3) Å^3, Z = 8, $R_{gt}(F)$ = 0.0351, $wR_{ref}(F^2)$ = 0.0402, T = 293 K.

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The structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Cutout of the $EuCr_2Al_{20}$ structure. Chromium and aluminum atoms are drawn as blue and magenta circles, respectively. The condensation pattern of the Eu@Al_{16} and Cr@Al_{12} polyhedra is emphasized. The left-hand drawing shows the chromium substructure.

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Table 1: Data collection and handling.

Crystal:	Silvery irregular shape
Size:	0.04 × 0.06 × 0.08 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	6.31 mm^{-1}
Diffractometer, scan mode:	IPDS Stoe
θ_{max}, completeness:	33.4°, 99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	16,086, 325, 0.119
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 267
$N(param)_{refined}$:	18
Programs:	X-Area [1], JANA2006 [2]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	x	y	z	U_{iso}*/U_{eq}
Eu1[a]	0.125	0.125	0.125	0.00870 (8)
Cr1	0.5	0.5	0.5	0.00697 (12)
Al1	0.05861 (4)	0.05861 (4)	0.32600 (5)	0.01114 (17)
Al2	0.48756 (7)	0.125	0.125	0.0088 (2)
Al3	0	0	0	0.0225 (3)

[a]Occupancy: 0.938 (5).

1 Source of material

The aluminum-rich phases EuT_2Al_{20} (T = Ti, V, Cr, Nb, Mo, Ta, W) were obtained by reaction of the elements using the aluminum self-flux technique [3]. Starting materials were

europium ingots (American Elements, 99.99%), titanium (Strem Chemicals, 99.7%), chromium (Alfa Aesar, 99.95%), niobium (Alfa Aesar, 99.6%), molybdenum (Ventron, 99.9%), tantalum (Strem Chemicals, 99.98%) and tungsten (Strem Chemicals, 99.95%) powder, vanadium sheet (Alfa Aesar, 99.7%) and aluminum turnings (Koch Chemicals, 99.9%). The elements were mixed in the atomic ratios Eu:*T*:Al = 1:2:40, placed in alumina crucibles and sealed in evacuated silica ampoules. The mixtures were heated to 1120 K at a rate of 50 K/h, kept for 300 h and finally cooled to room temperature at a rate of 6 K/h. The excess aluminum was dissolved in diluted hydrochloric acid.

2 Experimental details

The phase purity of the polycrystalline products was investigated by means of powder X-ray diffraction (Enraf-Nonius FR552 Guinier camera, imaging plate detector, Fujifilm BAS-1800 read-out system, Cu-$K_{\alpha 1}$ radiation and α-quartz (a = 491.30 and c = 540.46 pm) as an internal standard. The refined lattice parameter (1448.77(5) pm) agrees with the earlier study (1479.7(2) pm) [4]. $EuCr_2Al_{20}$ crystals were selected from the mechanically fragmented sample extracted from the aluminum flux. The crystal quality was tested through Laue photographs (Buerger camera, image plate detection system). Single crystal X-ray diffraction was performed at room temperature on a Stoe IPDS-II diffractometer (graphite monochromatized Mo-K_α radiation; oscillation mode). A numerical absorption correction was applied. The starting atomic parameters were deduced with the charge-flipping algorithm [5] implemented in Superflip [6] and the structure was refined on F^2 with the Jana2006 software package [2], with anisotropic displacement parameters for all atoms. Separate refinement of the occupancy parameters indicated a small degree of defects for the 8*a* europium site. This occupancy parameter was refined as least-squares variable in the final cycles, leading to the composition $Eu_{0.938(5)}Cr_2Al_{20}$ for the studied crystal. An EDX analyses of the crystal (5 ± 1% Eu: 11 ± 1% Cr: 84 ± 1% Al) confirmed the refined composition.

3 Comment

$EuCr_2Al_{20}$ crystallizes with the $CeCr_2Al_{20}$ type structure [7], space group $Fd\bar{3}m$ (the so-called diamond space group). The single crystal data fully confirm the previous studies [4, 8] based on powder X-ray diffraction. Although the $EuCr_2Al_{20}$ unit cell is large and comprises 184 atoms, it can easily be described with a condensation pattern of two Frank–Kasper [9, 10] polyhedra. From a geometrical point of view, the substructure build up by the europium and chromium atoms corresponds to the $MgCu_2$ type (cubic Laves phase). In the figure we present a cutout of the $EuCr_2Al_{20}$ structure. The left-hand part emphasizes the chromium substructure which consists of condensed Cr_4 tetrahedra with 513 pm d (Cr–Cr). The cavities left by the tetrahedral network are filled by the europium atoms which are surrounded by 16 aluminum atoms (4× Al3 and 12× Al1, see Table 3). These $Eu@Al_{16}$ polyhedra are condensed *via* common corners. The chromium atoms have 12 aluminum neighbors in icosahedral coordination and also these $Cr@Al_{12}$ polyhedra (6× Al2 and 6× Al1) are condensed *via* common corners (right-hand part of the figure). The Cr–Al distances in the $EuCr_2Al_{20}$ structure range from 257 to 280 pm and are larger than the sum of the covalent radii of 243 pm for Cr + Al [11]. The three crystallographically independent aluminum atoms show a broader range of Al–Al distances (271–311 pm). These are comparable with *fcc* aluminum (12 × 286 pm) [12]. A comment is appropriate for the slight europium deficiency (93.8(5)%) observed from the refinement of the occupancy parameters. Such defects have been observed in few of the $CeCr_2Al_{20}$ type phases, e.g. 95.8(3%) praseodymium occupancy in PrV_2Al_{20} [13]. Several of the $CeCr_2Al_{20}$ type phases have been studied with respect to *rattling* of the rare earth atom within the Al_{16} cage. Such anharmonic oscillations are favorable for thermoelectric materials, where suppression of the thermal conductivity enhances the thermoelectric efficiency.

Table 3: Interatomic distances (/pm) in the first coordination spheres of europium and chromium.

Eu:	4	Al3	314.5 (1)	Cr:	6	Al2	257.4 (1)
	12	Al1	322.2 (1)		6	Al1	279.9 (1)

$EuCr_2Al_{20}$ and the isotypic aluminides EuT_2Al_{20} with T = Ti, V, Nb, Ta, Mo and W were studied by ^{151}Eu Mössbauer spectroscopy at room temperature. The isomer shifts (Table 4) show a narrow range from −8.34(1) mm s^{-1} ($EuCr_2Al_{20}$) to −8.97(2) mm s^{-1} (EuW_2Al_{20}). The spectra gave no hint for any Eu(III) contribution. The isomer shift values are in the usual range observed for divalent europium intermetallics with pronounced covalent bonding. This is in close agreement with the magnetic behavior of these europium intermetallics [8, 14, 15]. The course of the isomer shifts shows no simple correlation with the valence electron count and the lattice parameter.

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Table 4: Fitting parameters for ^{151}Eu Mössbauer spectra of aluminides EuT_2Al_{20}. The measurements were carried out in transmission geometry with a $^{151}Sm:EuF_3$ source at room temperature. δ = isomer shift, Γ = experimental line width. Due to the cubic site symmetry of europium, no quadrupole splitting occurs. The lattice parameters and the valence electron count are listed for comparison.

Compound	δ/mm s^{-1}	Γ/mm s^{-1}	a/pm	VEC
$EuTi_2Al_{20}$	−8.77 (1)	2.49 (3)	1472.26 (5)	70
EuV_2Al_{20}	−8.58 (1)	2.43 (3)	1454.92 (7)	72
$EuNb_2Al_{20}$	−8.94 (1)	2.55 (4)	1478.3 (2)	72
$EuTa_2Al_{20}$	−8.94 (2)	2.50 (6)	1477.27 (9)	72
$EuCr_2Al_{20}$	−8.34 (1)	2.53 (2)	1448.77 (5)	74
$EuMo_2Al_{20}$	−8.54 (1)	2.50 (3)	1460.56 (6)	74
EuW_2Al_{20}	−8.97 (2)	2.51 (6)	1459.81 (4)	74

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Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

References

1. X-Area. *The Stoe Single Crystal Diffraction Software Package*; STOE & Cie GmbH: Darmstadt, Germany.
2. Petříček V., Dušek M., Palatinus L. Crystallographic computing system JANA2006: general features. *Z. Kristallogr*. 2014, *229*, 345–352.
3. Kanatzidis M. G., Pöttgen R., Jeitschko W. The metal flux – a preparative tool for intermetallic compounds. *Angew. Chem. Int. Ed.* 2005, *44*, 6996–7023.
4. Manyako M. B., Yahson T. L., Zarechnyuk O. S. Phase transformations in the Ca–V(Cr)–Al systems at 770 K. *Russ. Metall.* 1990, *2*, 199–201.
5. Palatinus L. The charge-flipping algorithm in crystallography. *Acta Crystallogr.* 2013, *B69*, 1–16.
6. Palatinus L., Chapuis G. SUPERFLIP – a computer program for the solution of crystal structures by charge flipping in arbitrary dimensions. *J. Appl. Crystallogr.* 2007, *40*, 786–790.
7. Krypyakevych P. I., Zarechnyuk O. S. The RCr_2Al_{20} compounds in the systems of the rare earth metals and calcium and their crystal structures. *Dopov. Akad. Nauk Ukr. RSR Ser. A* 1968, 364–367.
8. Thiede V. M. T., Jeitschko W., Niemann S., Ebel T. $EuTa_2Al_{20}$, $Ca_6W_4Al_{43}$ and other compounds with $CeCr_2Al_{20}$ and $Ho_6Mo_4Al_{43}$ type structures and some magnetic properties of these compounds. *J. Alloys Compd.* 1998, *267*, 23–31.
9. Frank F. C., Kasper J. S. Complex alloy structures regarded as sphere packings. I. Definitions and basic principles. *Acta Crystallogr.* 1958, *11*, 184–190.
10. Frank F. C., Kasper J. S. Complex alloy structures regarded as sphere packings. II. Analysis and classification of representative structures. *Acta Crystallogr.* 1959, *12*, 483–499.
11. Emsley J. *The Elements*; Oxford University Press: Oxford, 1999.
12. Donohue J. *The Structures of the Elements*; Wiley: New York, 1974.
13. Okuyama D., Tsujimoto M., Sagayama H., Shimura Y., Sakai A., Magata A., Nakatsuji S., Sato T. J. Crystal structure in quadrupolar Kondo candidate $PrTr_2Al_{20}$ (*Tr* = Ti and V). *J. Phys. Soc. Jpn.* 2019, *88*, 015001.
14. Swatek P., Kaczorowski D. Magnetic properties of $EuCr_2Al_{20}$. *J. Magn. Magn. Mater.* 2016, *416*, 348–352.
15. Ramesh Kumar K., Nair H. S., Bhattacharyya A., Thamizhavel A., Strydom A. M. Metamagnetism, sign reversal and low temperature magnetocaloric effect in single-crystalline EuV_2Al_{20}. *J. Magn. Magn. Mater.* 2018, *452*, 205–209.