

Crystal Structure of ErCd₃ and Its Isomorphous Compounds

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The crystal structure of ErCd₃ has been solved using photographic data. The compound is orthorhombic, $a=7.094$, $b=10.678$, $c=4.804$ Å, space group *Cmcm*, $Z=4$. The packing arrangement is closely related to that of GdCd₃, with the hexagonal Ni₃Sn structure type. All the MCd₃ compounds with M = Tb, Dy, Ho, Tm, Lu and Y are isotypic with ErCd₃.

During a study on the alloying behaviour of the rare-earth metals with cadmium (Bruzzone, Fornasini & Merlo, 1972), Tb, Dy, Ho, Er, Tm, Lu and Y were found to form isomorphous MCd₃ phases. The purpose of the present work was the determination of their crystal structure.

The preparation of the compounds is described by Bruzzone *et al.* (1972). Several, single needle-shaped crystals of ErCd₃ were examined with X-rays by Laue, rotating, Weissenberg and precession methods, using Cu or Mo $K\alpha$ radiation. The intensity data were obtained from a well formed prismatic crystal, measuring $0.2 \times 0.02 \times 0.02$ mm. Integrated precession photographs, taken with filtered Mo radiation, provided 217 independent reflexions of which 129 observed reflexions were measured by a microdensitometer and 88 unobserved were assumed to have a value equal to half the least observable intensity. Lorentz and polarization corrections were applied, but as the crystal was approximately cylindrical and $\mu r \approx 0.5$ for Mo radiation, no absorption correction was made.

All crystals showed orthorhombic symmetry and the lattice constants, subsequently refined from powder data, are:

$$a=7.094, \quad b=10.678, \quad c=4.804 \text{ \AA}.$$

The conditions for possible reflexions are: hkl present with $h+k=2n$, and $h0l$ present with $l=2n$, indicating the three possible space groups *Cmc2₁*, *C2cm* and *Cmcm*.

A pycnometric determination of the density gave a value $d_{\text{exp}}=9.1 \text{ g.cm}^{-3}$ which agrees with the calculated value $d_{\text{calc}}=9.21 \text{ g.cm}^{-3}$, based on four unit formulae per cell.

The comparison of the powder photographs of ErCd₃ with those of the hexagonal GdCd₃ phase (Ni₃Sn structure type, $a=6.621$, $c=4.933$ Å; Bruzzone, Fornasini & Merlo, 1971), shows a certain resemblance. The cell constants of ErCd₃ are related to Ni₃Sn-like GdCd₃ as follows: $a \approx a_{\text{hex}}$, $b \approx a_{\text{hex}}/3$ and $c \approx c_{\text{hex}}$. Moreover, it was noticed that the intensities of the spots hkl were equal to those of $h,k,l+2$, apart from the L_p factor and normal decline, suggesting that the atoms in the cell lie on two planes perpendicular to [001] at a distance of $c/2$. A trial structure in the *Cmcm*

space group, based on a simple orthorhombic distortion of the Ni₃Sn type, gave a reasonable agreement between calculated and observed intensities. A modified version of the program *ORFLS* (Busing, Martin & Levy, 1962), was used for the full-matrix least-squares refinement. The function minimized was $\sum_w (|F_o| - |KF_c|)^2$. In this calculation, amplitudes of 129 reflexions that were actually observed were given unit weight; those of reflexions too weak to be observed were given zero weight. The atomic scattering factors were corrected for the anomalous scattering with the values given in *International Tables for X-ray Crystallography* (1962). Eleven parameters were refined – four positional coordinates, six scale factors and an overall temperature factor. After a few cycles including all observed reflexions, an R value of 0.067 was obtained, where $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. At this stage it was observed that some strong reflexions, namely 002, 004, 006, 221 and 040, showed an observed structure factor lower than the calculated one. A secondary extinction correction was then applied, using the formula $|F_{\text{correct}}| = |F_o|(1 + gI_c)$ where I_c is the calculated intensity and g is a parameter to be determined empirically. Refinement proceeded assuming isotropic temperature factors for each atom as variables and gave a final R value of 0.060. For all reflexions the R value becomes 0.105. After the last cycle the shifts in the coordinates were nearly one per cent of their estimated standard deviations. In Table 1 are listed crystallographic data and parameters of ErCd₃ with the corresponding standard deviations. Table 2 collects the final observed and calculated structure factors. No attempt was made to refine further by using anisotropic temperature factors as variables, nor was refinement attempted using the space groups *Cmc2₁* and *C2cm*.

Table 1. Crystallographic data for ErCd₃

The estimated standard deviations from the least-squares refinements are given in parentheses in units of the last significant figure of the parameter value.

Space group: <i>Cmcm</i> (No 63)					
$a=7.094$, $b=10.678$, $c=4.804$ Å					
$d_{\text{exp}}=9.1 \text{ g.cm}^{-3}$; $d_{\text{calc}}=9.21 \text{ g.cm}^{-3}$.					
	Position	x	y	z	$B(\text{Å}^2)$
4 Er	4(c)	0	0.3679 (4)	$\frac{1}{4}$	0.40 (8)
4 Cd(1)	4(c)	0	0.8249 (8)	$\frac{1}{4}$	0.75 (13)
8 Cd(2)	8(g)	0.2129 (6)	0.0950 (5)	$\frac{1}{4}$	0.71 (10)

Table 2. Observed and calculated structure factors of ErCd₃

An asterisk indicates reflexions which were too weak to be measured.

h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c
0	2	0	290.0	3.6	2	6	1	229.9	225.1	6	4	2	195.3	138.6
0	4	0	444.9	454.8	2	8	1	44.2	63.2	8	0	2	109.2	141.9
0	6	0	316.4	382.0	2	10	1	49.6	111.6	8	2	3	51.5	62.2
0	8	0	100.8	86.2	2	12	1	56.8	76.6	0	2	3	41.3	59.4
0	10	0	112.8	105.2	2	14	1	62.2	68.1	0	4	3	282.0	279.3
0	12	0	50.0	43.9	3	3	1	30.0	22.9	0	6	3	45.5	42.4
0	14	0	42.4	35.2	3	5	1	44.3	94.8	0	8	3	262.0	260.0
1	1	0	39.5	27.3	3	7	1	41.4	41.0	0	10	3	79.1	86.6
1	3	0	22.4	16.5	3	9	1	200.0	216.6	0	12	3	125.7	116.6
1	5	0	141.1	163.9	3	11	1	96.0	42.5	1	1	3	34.1	51.6
1	7	0	171.4	175.9	3	13	1	224.8	254.6	1	3	3	121.3	131.3
1	9	0	136.2	115.4	4	2	1	125.6	147.9	1	5	3	38.6	59.8
1	11	0	236.0	213.0	4	4	1	232.8	224.0	1	7	3	178.2	153.1
1	13	0	43.1	16.3	5	1	1	146.3	140.3	1	9	3	125.0	129.3
2	0	0	102.8	112.4	5	3	1	226.1	297.0	1	11	3	83.0	116.8
2	2	0	203.0	213.4	6	2	1	226.7	253.2	1	13	3	104.0	128.6
2	4	0	66.1	68.7	6	4	1	94.6	86.7	2	2	3	410.1	442.2
2	6	0	120.1	124.2	6	6	1	46.1	62.1	2	4	3	40.9	54.4
2	8	0	124.9	60.0	8	2	1	207.0	214.0	2	6	3	195.1	187.5
2	10	0	209.3	262.0	8	4	2	131.7	127.0	2	8	3	51.7	51.8
2	12	0	107.4	129.4	8	6	2	14.2	2.4	2	10	3	57.5	112.0
3	1	0	237.1	231.6	0	2	2	399.3	414.5	3	1	3	41.3	44.4
3	3	0	43.8	68.0	0	4	2	41.4	50.1	3	3	3	44.4	44.6
3	5	0	293.0	332.3	0	6	2	48.6	38.8	3	5	3	232.5	227.4
3	7	0	39.7	64.1	0	8	2	78.4	95.7	3	7	3	54.1	52.6
3	9	0	217.0	200.1	0	10	2	36.6	47.2	3	9	3	193.0	217.4
3	11	0	95.1	95.2	0	12	2	36.6	47.2	3	11	3	61.1	37.6
3	13	0	61.8	5.3	0	14	2	41.7	15.6	4	1	3	184.9	153.7
4	0	0	432.4	470.0	1	3	2	38.5	20.0	4	2	3	128.1	124.5
4	2	0	105.1	104.1	1	5	2	187.2	153.3	5	1	3	114.0	119.4
4	4	0	315.3	307.8	1	7	2	187.2	153.3	5	3	3	215.6	216.2
4	6	0	180.1	180.1	1	9	2	187.2	153.3	5	5	3	221.0	216.6
4	8	0	180.1	180.1	1	11	2	211.0	216.9	6	2	3	176.7	168.6
4	10	0	157.0	158.1	2	3	2	187.0	170.5	6	4	3	444.3	440.3
4	12	0	157.0	158.1	2	5	2	187.0	170.5	6	6	3	59.4	59.1
4	14	0	157.0	158.1	2	7	2	187.0	170.5	6	8	3	203.0	204.1
4	16	0	157.0	158.1	2	9	2	187.0	170.5	6	10	3	48.1	39.5
4	18	0	157.0	158.1	2	11	2	187.0	170.5	6	12	3	75.0	51.3
0	0	2	176.8	68.7	2	10	2	201.8	187.2	0	0	4	42.1	27.8
0	0	4	339.2	359.1	2	12	2	209.2	201.7	0	0	6	42.1	27.8
0	0	6	137.8	43.2	3	1	2	32.0	32.0	0	0	8	39.8	22.5
0	0	8	137.8	43.2	3	3	2	32.0	32.0	0	0	10	42.7	36.9
0	0	10	130.8	67.2	3	5	2	310.3	296.2	1	3	4	145.2	121.0
0	0	12	130.8	67.2	3	7	2	434.0	411.9	1	5	4	92.7	64.6
0	0	14	117.5	172.1	3	9	2	168.6	183.8	1	7	4	175.5	178.8
1	1	1	176.2	172.1	3	11	2	434.0	411.9	1	9	4	109.4	110.8
1	1	3	204.8	226.8	3	13	2	64.5	5.9	1	11	4	175.5	178.8
1	1	5	177.1	181.0	4	2	2	42.1	30.9	1	13	4	40.8	13.8
1	1	7	218.8	233.0	4	4	2	42.1	30.9	1	15	4	52.8	38.8
1	1	9	185.5	189.3	4	6	2	36.7	13.4	2	2	4	154.4	124.6
1	1	11	11	82.1	5	1	2	72.2	86.9	2	4	4	54.6	35.8
1	1	13	148.4	144.7	5	3	2	36.7	13.4	2	6	4	244.8	236.6
2	2	1	624.1	181.4	6	0	2	207.9	200.9	2	8	4	58.8	31.2
2	2	3	175.9	2.4	6	2	2	49.1	73.4	2	10	4	144.2	151.3

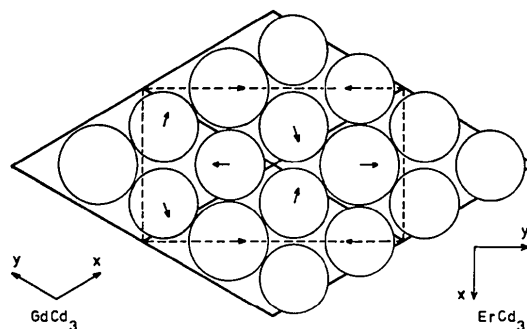


Fig. 2. Geometrical relation between the GdCd₃ (Ni₃Sn-type) and ErCd₃ structures. Section *xy* at *z* = 1/4. Large circles are rare earth atoms, small circles Cd atoms. Four GdCd₃ cells are drawn with solid lines; the dashed lines limit the ErCd₃ cell.

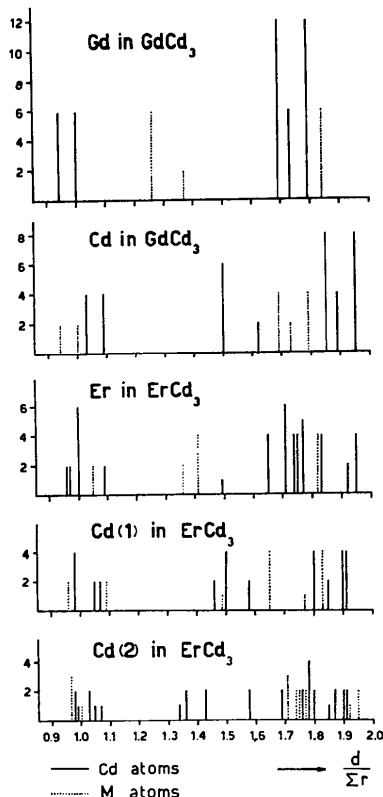


Fig. 3. Atomic distribution around the rare earth and cadmium atoms in GdCd₃ and ErCd₃.

The crystal-structure determination was carried out also for the isomorphous compound YCd₃. Intensity data were collected from a crystal measuring 0.13 × 0.03 × 0.04 mm using the same procedure as for ErCd₃. A least-squares refinement was made with only 53 observed reflexions, starting with the positional parameters of ErCd₃, single isotropic *B* factors and one scale factor. An *R* value of 0.066 was obtained at the end of the last cycle. In Table 3 are shown crystallographic data for YCd₃.

Table 3. Crystallographic data for YCd₃

Space group: *Cmcm* (No. 63)
a = 7.044, *b* = 10.864, *c* = 4.837 Å
*d*_{exp} = 7.6 g.cm⁻³; *d*_{calc} = 7.64 g.cm⁻³.

	Position	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)
4 Y	4(<i>c</i>)	0	0.368 (3)	1/4	1.5 (9)
4 Cd(1)	4(<i>c</i>)	0	0.822 (2)	1/4	0.8 (5)
8 Cd(2)	8(<i>g</i>)	0.216 (2)	0.094 (2)	1/4	0.6 (3)

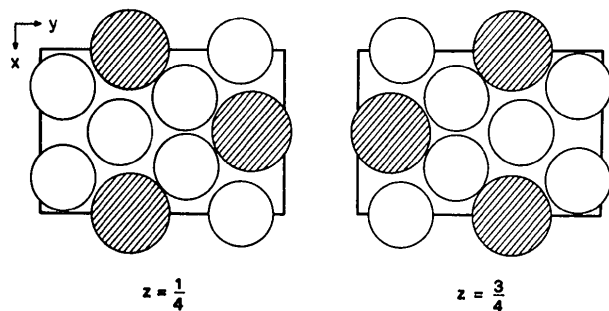


Fig. 1. The two layers at *z* = 1/4 and *z* = 3/4 of the elementary cell of ErCd₃. Shaded circles: Er; open circles: Cd.

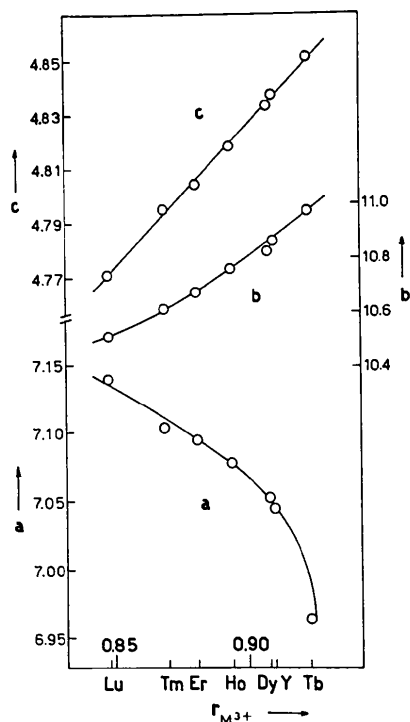
Fig. 1 shows the two layers at *z* = 1/4 and *z* = 3/4 of the elementary cell of ErCd₃. In Table 4 are reported the interatomic distances for ErCd₃ and YCd₃. The very close relationship between the GdCd₃ and ErCd₃ structures is shown in Fig. 2. The arrows indicate the shifting directions of the atoms going from the hexagonal to the orthorhombic packing. In the GdCd₃ and ErCd₃ structures the coordination around the rare earth and cadmium atoms is somewhat different. This can be shown by plotting, for each atom in the asym-

metric unit, the number of atoms at equal distance *vs.* $d/\sum r$, where d is the corresponding distance and $\sum r$ is the sum of the metallic radii of the considered atom and the surrounding one. As already noted by Bruzzone, Fornasini & Merlo (1970), in all cases a gap in this atomic distribution occurs. The coordination numbers obtained by counting all the atoms before the gap are generally in good agreement with the values obtained following the Frank & Kasper (1958, 1959) criterion. Fig. 3 shows the atomic distribution plot for GdCd₃ and ErCd₃. In GdCd₃ the Gd atom is surrounded by twelve Cd atoms, six at the same distance and six at a different distance. In ErCd₃ the coordination number of the rare-earth atom increases to 14 because an Er atom is bound with 12 Cd atoms and with two Er atoms. Regarding the two crystallographic types of cadmium in ErCd₃, their coordination numbers are 12 and 11, compared with the value of 12 shown by the Cd atom in GdCd₃.

Table 4. *Interatomic distances for ErCd₃ and YCd₃*

ErCd ₃		YCd ₃	
Er-2 Er	3.705 Å	Y-2 Y	3.76 Å
Er-2 Cd(1)	3.577	Y-2 Cd(1)	3.56
Er-2 Cd(1)	3.164	Y-2 Cd(1)	3.18
Er-2 Cd(2)	3.283	Y-2 Cd(2)	3.34
Er-2 Cd(2)	3.167	Y-2 Cd(2)	3.17
Er-4 Cd(2)	3.174	Y-4 Cd(2)	3.17
Cd(1)-2 Er	3.577	Cd(1)-2 Y	3.56
Cd(1)-2 Er	3.164	Cd(1)-2 Y	3.18
Cd(1)-2 Cd(2)	3.257	Cd(1)-2 Cd(2)	3.32
Cd(1)-2 Cd(2)	3.190	Cd(1)-2 Cd(2)	3.18
Cd(1)-4 Cd(2)	2.964	Cd(1)-4 Cd(2)	3.00
Cd(2)-1 Er	3.283	Cd(2)-1 Y	3.34
Cd(2)-1 Er	3.167	Cd(2)-1 Y	3.17
Cd(2)-2 Er	3.174	Cd(2)-2 Y	3.17
Cd(2)-1 Cd(1)	3.257	Cd(2)-1 Cd(1)	3.32
Cd(2)-1 Cd(1)	3.190	Cd(2)-1 Cd(1)	3.18
Cd(2)-2 Cd(1)	2.964	Cd(2)-2 Cd(1)	3.00
Cd(2)-1 Cd(2)	3.022	Cd(2)-1 Cd(2)	3.05
Cd(2)-2 Cd(2)	3.145	Cd(2)-2 Cd(2)	3.17

The lattice constants of the orthorhombic MCd₃ phases, subsequently calculated, are reported by Bruzzone *et al.* (1972), who noted that the cube root of the cell volume *vs.* the rare earth trivalent ionic radius shows a regularly decreasing linear trend from TbCd₃ to LuCd₃. But, if the single lattice constants of these compounds are plotted *vs.* the same abscissa (Fig. 4), a decreasing trend is observed for the *b* and *c* constants, while the *a* constant shows an increasing trend. The inclination to form a shorter M-M distance between rare earth atoms is probably the reason for this abnormal behaviour. In fact, with decreasing rare-earth atomic dimensions, the lengthening of the elementary

Fig. 4. Lattice constants of the orthorhombic MCd₃ phases (in Å) *vs.* the rare earth trivalent ionic radii.

cell in the *x* direction makes possible a large reduction in the *b* constant, which is necessary for keeping the M-M distance short.

Apart from the stoichiometry, the atomic positions of ErCd₃ are quite similar to those of NaHg.

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