SHORT STRUCTURAL PAPERS

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Dy_5Ru_2 and Y_5Ru_2 with Mn_5C_2-Type Structure

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Abstract. Dy_5Ru_2, monoclinic, $C2/c$, $Z = 4$, a = 15·658 (1), b = 6·2899 (2), c = 7·2584 (3) Å, $\beta = 97{\cdot}25$ (1)°, $D_x = 9{\cdot}50$ Mg m^{-3}. The compound crystallizes with the Mn_5C_2 (Pd_5B_2) structure type. The structure was refined from single-crystal data. Final $R = 0{\cdot}058$ for 932 counter intensities. Y_5Ru_2, a = 15·769 (6), b = 6·341 (2), c = 7·320 (3) Å, $\beta = 97{\cdot}20$ (4)°, $D_x = 5{\cdot}91$ Mg m^{-3}. The structure is of the same type as Dy_5Ru_2. A discussion of the coordination is given.

Introduction. Loebich & Raub (1976) published the phase diagrams of the systems Gd–Ru and Dy–Ru. They reported three new phases of approximate compositions R_3Ru, $R_{73}Ru_{27}$ and R_2Ru in the rare-earth-rich part of the phase diagram and synthesized the corresponding Y-containing compounds in order to study their magnetic properties. Palenzona (1979) recently identified the first two phases as being isostructural with Fe_3C and Mn_5C_2, respectively, and found isotypic Ru-containing phases with La, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm and Lu. This work, based on powder photographs, is supplemented here by the results of a single-crystal study of one particular compound, Dy_5Ru_2, and by the determination of the cell parameters of Y_5Ru_2.

The Mn_5C_2-type structure has been found for other rare-earth–late-transition-metal compounds such as R_5Co_2 (R = Pr, Nd and Sm; Moreau & Paccard, 1976), R_5Ir_2 (R = Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Lu and Y; Le Roy, Paccard & Moreau, 1980), Eu_5Pd_2 and Yb_5Pd_2 (Iandelli & Palenzona, 1973, 1974) and Yb_5Pt_2 (Iandelli & Palenzona, 1975). Single-crystal studies have been published for Sm_5Co_2 and Lu_5Ir_2.

Dy_5Ru_2: Samples were prepared from Dy ingots (99·5 wt%) and Ru powder (99·9 wt%) by arc melting under an Ar atmosphere. Annealing was not necessary as a single crystal could be directly isolated from the crushed melt. The C-centred monoclinic cell, determined on an automatic diffractometer, and the systematic absences ($h0l$ present only for $l = 2n$) indicating space group Cc or $C2/c$, confirm the Mn_5C_2-type structure. The cell parameters given in the *Abstract* were refined from the 2θ values of 17 independent reflections. Data were collected on a four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation in the $\theta/2\theta$ scan mode out to $\sin\theta/\lambda = 0{\cdot}70$ Å^{-1}. All computer programs used for the data reduction and refinement were those of the XRAY system (1976). In spite of the irregular shape of the crystal an absorption correction assuming spherical shape was applied, the numerical values for $\mu R = 0{\cdot}9$ being taken from *International Tables for X-ray Crystallography* (1967). Correction factors for anomalous dispersion were taken from *International Tables for X-ray Crystallography* (1974) and relativistic Hartree–Fock scattering factors from Cromer & Mann (1968). With an isotropic secondary-extinction correction, the refinement converged at $R = 0{\cdot}058$ for 932 contributing reflections with

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$|F_o| > 3\sigma_{F_o}$. Final positional and isotropic thermal parameters are given in Table 1.†

Y_5Ru_2: The starting materials used were Y ingots (99·5 wt%) and Ru powder (99·9 wt%). A sample containing 29 at.% Ru was prepared in an arc furnace under an Ar atmosphere. A powder photograph, taken on a Guinier–Nonius camera with Cu $K\alpha$ radiation and with Si as standard, indicated a Mn_5C_2-type structure. The reflections were indexed by comparison with a simulated powder pattern calculated with *LAZY PULVERIX* (Yvon, Jeitschko & Parthé, 1977) assuming the fractional coordinates determined for Dy_5Ru_2. A least-squares refinement of the 2θ values of 18 reflections was applied in the evaluation of the cell parameters and e.s.d.'s.

A second sample with 27 at.% Ru, the composition proposed by Loebich & Raub (1976), has already been shown to exhibit the diffraction lines of Y_3Ru of an Fe_3C type (Sanjines-Zeballos, Chabot & Parthé, 1980). The Mn_5C_2-type phase in equilibrium with Y_3Ru has slightly smaller lattice constants [$a = 15{\cdot}72\,(1)$, $b = 6{\cdot}320\,(3)$, $c = 7{\cdot}296\,(5)$ Å, $\beta = 97{\cdot}22\,(5)°$] indicating a certain number of vacant structure sites.

Discussion. In the Fe_3C, Mn_5C_2, Th_7Fe_3 and other structure types found in the rare-earth-rich part of the R–T systems, where T is a metal from the Fe, Co or Ni groups, the transition-metal atom is generally considered to be in the centre of a trigonal prism of rare-earth atoms. The different ways of linking these prisms together have been discussed in several publications. It seemed of interest here to study the actual shapes of the individual prisms. In the Fe_3C and Mn_5C_2 types, the two competing types in the Dy–Ru system up to 30% Ru, there is a rare-earth atom outside each rectangular prism face. These three extra atoms (denoted as Dy*) belong to the coordination polyhedra as defined by Frank & Kasper (1958). Fig. 1 shows the resultant tricapped trigonal prism formed by the Dy atoms surrounding each Ru atom. The distances given in Fig. 1 for the refined structure of Dy_5Ru_2 are compared in Fig. 2 with those found in Dy_5Ir_2, assuming the same fractional coordinates as in Lu_5Ir_2 (Le Roy, Paccard & Moreau, 1980), and with the corresponding distances calculated for Dy_3Ru and Dy_3Ir, using the coordinates refined for Sm_3Ir (Le Roy, Moreau, Paccard & Parthé, 1979) in both cases. It will be seen that there is no evident gap in the Ru(Ir)–Dy distance histograms for the two Mn_5C_2-type structures and that the transition metal ought to be considered as at least seven-coordinated instead of six-coordinated. This is especially pronounced in Dy_5Ir_2 where the distance to the seventh-nearest atom to Ir has about the same value as the distance to the sixth-nearest atom belonging to the trigonal prism. As a consequence of this short T–Dy* distance the rectangular face capped by the Dy* atom beomes larger and distorted; the three longest Dy–Dy distances correspond to sides of this face.

The trigonal prism as a construction unit is more readily recognizable in the Fe_3C-type structure since the six T–R distances are very similar and are followed by a gap in the histogram. Since the central T atom lies in a special position of symmetry m, the prism is less irregular. Thus, the two triangular faces of the prism

Table 1. *Fractional coordinates for* Dy_5Ru_2 *with the* Mn_5C_2 *structure type (space group* $C2/c$*)*

The e.s.d.'s are given in parentheses. The Debye–Waller factor is defined as $\exp[-2\pi^2\,10^{-2}U(2\sin\theta/\lambda)^2]$.

	Equipoint	x	y	z	U(Å²)
Dy(1)	8(f)	0·0932 (1)	0·1162 (2)	0·4160 (2)	1·18 (4)
Dy(2)	8(f)	0·2177 (1)	0·5766 (3)	0·3143 (2)	1·13 (4)
Dy(3)	4(e)	0	0·5838 (4)	0·25	0·99 (6)
Ru	8(f)	0·1100 (2)	0·2889 (4)	0·0761 (4)	1·33 (8)

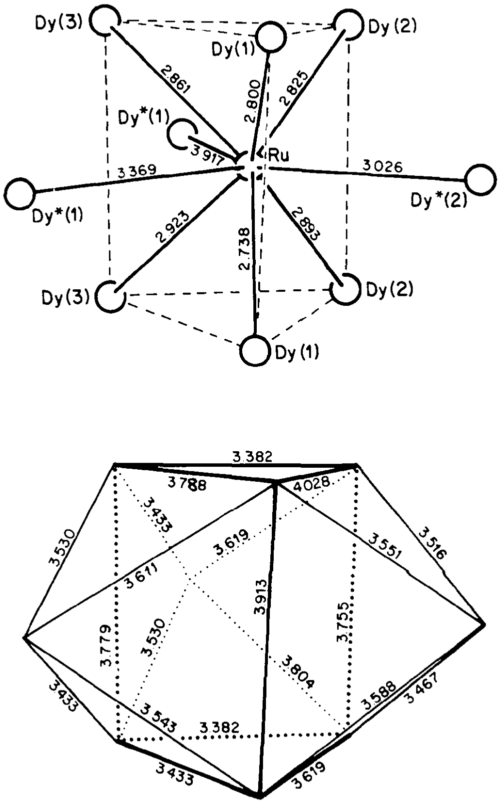

Fig. 1. Coordination polyhedron of Ru in Dy_5Ru_2. Starred Dy atoms cap the rectangular faces of the trigonal prism. Errors on interatomic distances are <0·004 Å.

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† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35145 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

itself are isosceles, the unique side being the shortest. One triangular face is considerably larger than the other; the two longest Dy—Dy distances correspond to the equal sides of this triangle and the third-longest distance to the vertical edge of the prism from the intersection of these sides. No significant differences can be seen between the Ru- and Ir-containing compounds but, as already mentioned, the same fractional coordinates have been used in the calculation of the distances for these structures.

Several methods have been proposed to calculate weighted coordination numbers (WCN). Brunner & Schwarzenbach (1971), for example, plot a histogram of the distances d_n from the chosen atom to surrounding atoms. For most structures a gap appears in the histogram of distances between, say, atom N and atom $N+1$. All atoms up to atom N are considered to belong to the coordination polyhedron. The weighted coordination number can then be calculated from:

$$\mathrm{WCN} = \sum_{n=1}^{N} \frac{d_{N+1} - d_n}{d_{N+1} - d_1}. \tag{1}$$

Brunner (1977) later suggested another weighting scheme based on reciprocal distances:

$$\mathrm{WCN} = \sum_{n=1}^{N} \frac{\dfrac{1}{d_n} - \dfrac{1}{d_{N+1}}}{\dfrac{1}{d_1} - \dfrac{1}{d_{N+1}}}. \tag{2}$$

Unfortunately for the structures discussed above, there are no clearly defined gaps in the histograms of the distances around the transition-metal atoms. The largest gaps in Dy_5Ru_2, Dy_5Ir_2 and Dy_3Ir are between d_8 and d_9; however, in Dy_3Ru the gap occurs between d_9 and d_{10}. More-clearly defined gaps are observed when the histograms are made with distances normalized to the sums of the atomic radii, as has been proposed by Bruzzone, Fornasini & Merlo (1971). With this modification the gap appears after the ninth-nearest neighbour, the tenth being a transition-metal atom with a radius about 25% smaller than those of the rare-earth atoms. For this reason, in all four compounds the first nine neighbours have been assumed to form the coordination polyhedron and have been considered in the calculation of the weighted coordination numbers given in the first two columns of Table 2.

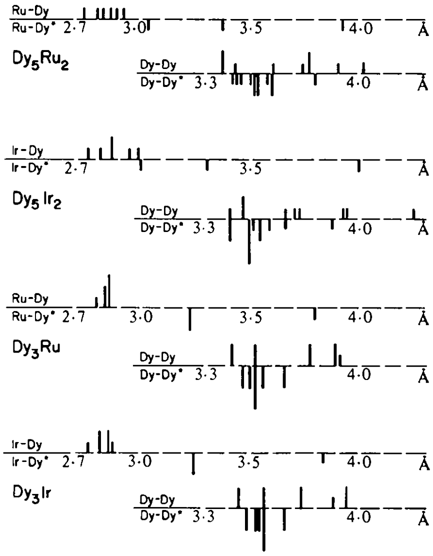

Fig. 2. Distance histograms for Dy_5Ru_2, Dy_5Ir_2 (Mn_2C_2-type structure) and Dy_3Ru, Dy_3Ir (Fe_3C-type structure). Only the distances within the tricapped trigonal prism shown in Fig. 1 are considered.

Table 2. *Weighted coordination numbers of the transition-metal atoms, calculated according to three different methods*

	Equation (1)	Equation (2)	Equation (3)
Dy_5Ru_2	7·35	6·87	6·78
Dy_5Ir_2	7·41	6·94	6·70
Dy_3Ru	7·68	7·31	7·22
Dy_3Ir	7·47	7·04	7·16

The third column of Table 2 contains the WCN calculated with a method proposed by O'Keeffe (1979) who considers the Voronoi polyhedron with N faces around the central atom and attributes weights proportional to the solid angles, S_n, subtended by the different faces at the central atom. Let S_1 be the largest solid angle, then O'Keeffe's WCN is given by

$$\mathrm{WCN} = \sum_{n=1}^{N} \frac{S_n}{S_1} = \frac{4\pi}{S_1}. \tag{3}$$

It should be noted in (3) that the closest atom does not necessarily subtend the largest solid angle, and that the number of faces is not important for the calculation of the coordination number. These facets of O'Keeffe's definition seem curious. The same problems may arise as with the gap method when the coordination polyhedron is formed of atoms of different sizes as the atomic radii of the different atoms have not been taken into account in calculating the WCN.

It can be seen from Table 2 that the coordination numbers calculated with (3) are close to those calculated with (2). All three methods of calculating the WCN indicate that the transition-metal atom has a higher coordination in the Fe_3C-type than in the Mn_5C_2-type compounds. There appears to be no significant difference between the Ru- and Ir-containing compounds.

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Structure of Potassium Arsenate $K_5As_3O_{10}$

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Abstract. $K_5As_3O_{10}$, orthorhombic, $P2_12_12_1$, a = 7·98 (1), b = 7·97 (1), c = 19·30 (2) Å, V = 1227·5 Å^3, Z = 4, D_m = 3·06, D_c = 3·14 Mg m^{-3}, μ(Mo $K\alpha$, λ = 0·7107 Å) = 10·5 mm^{-1}. The structure was solved by Patterson methods from X-ray single-crystal data. For 912 independent intensity data the final R = 0·04. Each As atom is tetrahedrally surrounded by four O atoms. Groups of three corner-sharing tetrahedra form strongly bent chains. The coordination number of the K atoms varies from six to nine. Tetragonal pseudosymmetry may lead to twinning.

Introduction. Structural data on potassium arsenates are needed for a study on As-containing silicate glasses (Verweij, 1979). Condensed alkali arsenates generally contain chains or rings of corner-sharing AsO_4 tetrahedra. $(LiAsO_3)_x$ (von Hilmer & Dornberger-Schiff, 1956) and $(NaAsO_3)_x$ (Liebau, 1956) contain chains of infinite length, whereas $Na_4As_2O_7$ (Leung & Calvo, 1973) contains pyroarsenate groups, built up from two AsO_4 tetrahedra.

Compounds similar to the title compound are $Na_5As_3O_{10}$ (Thilo & Winkler, 1966) of unknown crystal structure, $Na_5P_3O_{10}$ (Corbridge, 1960) containing stretched chains of three tetrahedra, and $H_5As_3O_{10}$ (Jost, Worzala & Thilo, 1966) which contains ribbons consisting of AsO_4 tetrahedra and AsO_6 octahedra.

The phase diagram of the K_2O–As_2O_5 system (Levin, Robbins & McMurdie, 1964) shows four compounds which are stable at room temperature: α-K_3AsO_4, $K_4As_2O_7$, $K_5As_3O_{10}$ and γ-$KAsO_3$. The title compound, $K_5As_3O_{10}$, melts incongruently at 903 K.

Single crystals were grown from a melt in a Pt–10% Rh crucible by cooling from 1073 K at a rate of 0·14 K min^{-1}. The composition of the melt was 58 mol% K_2O and 42 mol% As_2O_5, which is between that of $K_5As_3O_{10}$ and the eutectic between γ-$KAsO_3$ and $K_5As_3O_{10}$ (Levin, Robbins & McMurdie, 1964), so that the title compound was the primary crystalline phase on cooling. The cooled mixture consisted of microscopic needles of γ-$KAsO_3$ (Thilo & Dostál, 1959; Grunze, Dostál & Thilo, 1959) and transparent, highly imperfect crystals of $K_5As_3O_{10}$. The crystals were very hygroscopic and had to be handled in a glove bag filled with nitrogen (I^{2}R, Cheltenham, PA, USA). An irregular beam-shaped crystal of dimensions 0·32 × 0·20 × 0·08 mm was sealed in a glass capillary

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