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Preparation and Double-Helix Icosahedra Structure of δ-Co_2Zn_{15}

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The first known example of a regular face-sharing icosahedra helix is presented in the novel crystal structure of δ-Co_2Zn_{15}, solved and refined from single-crystal X-ray and neutron powder diffraction data. The compound δ-Co_2Zn_{15} is also the first example of an intermetallic compound crystallizing in the acentric hexagonal space group $P6_2$. The parameters from the single crystal refinement are $a = 11.292(2)$ Å, $c = 7.750(1)$ Å, $Z = 4$, and $R_w = 0.025$. © 2002 Elsevier Science (USA)

Key Words: **intermetallic compounds; zinc–cobalt; structure determination; synthesis design.**

INTRODUCTION

If regular polyhedra helices are taken to denote helices formed by the face sharing of non-intersecting platonic solids, there are, apart from trivial linear cases, only eight such geometrical objects; one formed by the tetrahedron, the cube, and two each for the octahedron, the dodecahedron and the icosahedron, respectively (1). One of the dodecahedra helices approximates a close packing of dodecahedra, and suffers from the frustration caused in such a packing. Frustration also prohibits the realization of one of the octahedra helices, leaving only six chemically realizable structures. In all those cases, with the exception of the cube helix, the pitch of the helix is an irrational multiple of the polyhedra, and hence, slight distortions of the ideal structure are necessary in order to accommodate the helices in a periodic lattice. The occurrence of regular helices of tetrahedra has been noted in β-manganese (2) and in $BaCd_{13}$ (3), the cube helix occurs in CsCl and one of the dodecahedra helices occurs in chlartrate IV (4), but we have, until now, not been able to identify any representatives for the realizable octahedron helix, or for any of the icosahedra cases. We report here on what we believe to be the first example of a regular icosahedra helix. This is found in the compound δ-Co_2Zn_{15}. The novel crystal structure of δ-Co_2Zn_{15} is reported here as part of a project to investigate the structures of Zn-rich binary compounds formed with transition metals. The interest in the chemistry of zinc intermetallics has seen a revival in the last few years with several reported novel crystal structures (5, 6 and references therein).

EXPERIMENTAL

The synthesis of single crystals of δ-Co_2Zn_{15} was made with the melt–centrifugation method devised by Boström (7, 8). With this method, single crystals are grown on the high- melting reactant, in a melt richer in the low-melting reactant, which acts as a self-flux. The reaction takes place in an evacuated tube with a filter fixed at one end. The tube is kept inside an insulating steel container in the furnace. During the reaction, the whole assemblage is kept with the filter end raised, so that the reaction mixture is in the filter-less end of the tube. At the end of the reaction, the steel container is turned upside down and the melt is filtered away through the filter aided by centrifugal force. On top of the filter remain single crystals of the compound stable with the melt at the reaction temperature.

Zinc pellets (99.9%) weighing 1.88 g and 0.10 g of cobalt powder (99.9%) were pressed into a pellet and placed into a quartz ampoule prepared as described earlier. The assemblage was heated at 700°C for 48 h. Rod-shaped single crystals of up to 5 mm length were found on top of the filter

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after centrifugation. The crystals had a silvery luster and were hard and brittle. They could be cut without any visible deformation. The edges were sharply defined. The composition of the crystals was 14 ± 3 at% Co from EDX.

A powder sample for neutron diffraction was prepared by heating 9.004 g of zinc pellets (99.9%) and 1.119 g of cobalt powder (99.9%) at 700°C for 18 h inside an evacuated quartz tube. The sample was ground into a fine powder and pressed into pellets. The pellets were reheated at 700°C for 50 h inside an evacuated quartz tube. The sample was quenched in cold water and ground into a powder for the neutron-diffraction experiment.

X-Ray Diffraction

The single-crystal X-ray data were collected on an STOE IPDS, and the measurement details are given in Table 1. The space group $P6_2$ was uniquely determined from the Laue symmetry $P6/m$ and from the systematic extinctions ($00l$, $l = 3n$ allowed). The absolute configuration of the structure could not be determined with certainty, and the possibility that the structure crystallizes in the enantiomorphic space group $P6_4$ cannot be excluded. The structure was solved using direct methods (9), and refined using the software package JANA98 (10). There were no clear indications for the distinction between zinc and cobalt. Therefore, all the atoms were refined with the scattering factors for zinc. Structural parameters are given in Table 2.

TABLE 1
Details of the X-Ray Single-Crystal Experiment

Crystal data	
Chemical formula	Co_2Zn_{15}
Crystal system	Hexagonal
Space group	$P6_2$ (171)
Z	4
a (Å)	11.292(2)
c (Å)	7.750(1)
V(Å^3)	855.9
Density calc. (g cm^{-3})	7.51
Crystal form	Irregular
Crystal size (mm)	0.1 × 0.1 × 0.1
Color	Lustrous metallic
Absorption coeff. (mm^{-1})	39.3
Data collection	
Diffractometer	Stoe IPDS
Radiation	Mo$K\alpha$
No. of refls. measured	6691
No. of independent refls.	1119
No. of observed refls.	798
Observation crit.	$I > 3\sigma(I)$
Absorption corr.	Numerical from crystal shape
$T_{\min}$, $T_{\max}$	0.0287, 0.1122
R_{int}	0.06
Range of $h\,k\,l$	$-13 < h < 13$ $-13 < k < 13$ $-9 < l < 9$
Temperature (K)	298
Refinement	
Refinement of	F
No. of refls. used	1119
No. of parameters	92
Weighting scheme	$1/(\sigma^2 F) + 0.0001F^2)$
R, R_w	0.027, 0.025
S	1.15
$\Delta/\sigma_{\max}$	0.0002
$\Delta\rho_{\min}$, $\Delta\rho_{\max}$ (e Å^{-3})	−1.75, 2.24

TABLE 2
Coordinates and Thermal Parameters for δ-Co_2Zn_{15}, as Refined from the X-Ray Single-Crystal Data

Atom	Wyck.	Occ.	x	y	z	U_{eq} (Å^2)
Co_1[a]	6c	1	0.4245(2)	0.1402(2)	0.232851	0.0158(6)
Co_2/Zn_2[a]	3a	1	0	0	0.237(1)	0.0141(9)
Zn_3	6c	1	0.4242(1)	0.1556(2)	−0.1074(4)	0.0097(7)
Zn_4	6c	1	0.4827(1)	0.3715(1)	0.0945(6)	0.0110(7)
Zn_5	6c	1	0.2277(1)	0.1605(2)	0.0816(6)	0.0149(6)
Zn_6	6c	1	0.1902(2)	−0.0283(2)	0.3909(6)	0.0144(6)
Zn_7	6c	1	0.6612(1)	0.2782(1)	0.0694(6)	0.0122(6)
Zn_8	6c	1	0.4270(1)	0.1139(2)	0.5641(6)	0.0113(6)
Zn_9	6c	1	0.2429(1)	−0.0695(1)	0.0698(7)	0.0149(6)
Zn_{10}	6c	1	0.6250(1)	0.1086(1)	0.3627(7)	0.0109(7)
Zn_{11}	3a	1	0.5	0	0.0662(7)	0.0132(8)

[a] No distinction was made between zinc and cobalt in the X-ray single-crystal refinement.

Neutron Powder Diffraction

Neutron diffraction was carried out at the Studsvik Neutron Research Laboratory in Sweden in order to determine the positions of the cobalt atoms in the δ-Co_2Zn_{15} structure. The constant wavelength $\lambda = 1.4700$ Å was achieved with a double copper (220) monochromator. The detector bank consisted of 35 He-3 counters, and corresponding Soller collimators, with an angular divergence of 10 arc min. The diffraction pattern was measured from 4 to 140° 2θ with the increment of 0.080°. The Rietveld refinement was performed with the program Fullprof (11). The observed diffraction pattern, the calculated pattern and the difference curve are shown in Fig. 1. The crystal structure refined from the X-ray single-crystal data was used as a starting model. The scale factor, the background, the Gaussian profile function, the cell parameters, the coordinates, common temperature parameters for cobalt and zinc, respectively, and mixed occupancy parameters for Co_2/Zn_2 were refined; in total, 43 parameters. The agreement factors were $wR_p = 0.084$, $R_p = 0.075$, $R_{\text{Bragg}} = 0.023$, and $\chi^2 = 1.47$. No traces of any impurity phases could be observed in the diffraction pattern. The refined coordinates, given in Table 3, agree within 0.07 Å with those of the starting model. The

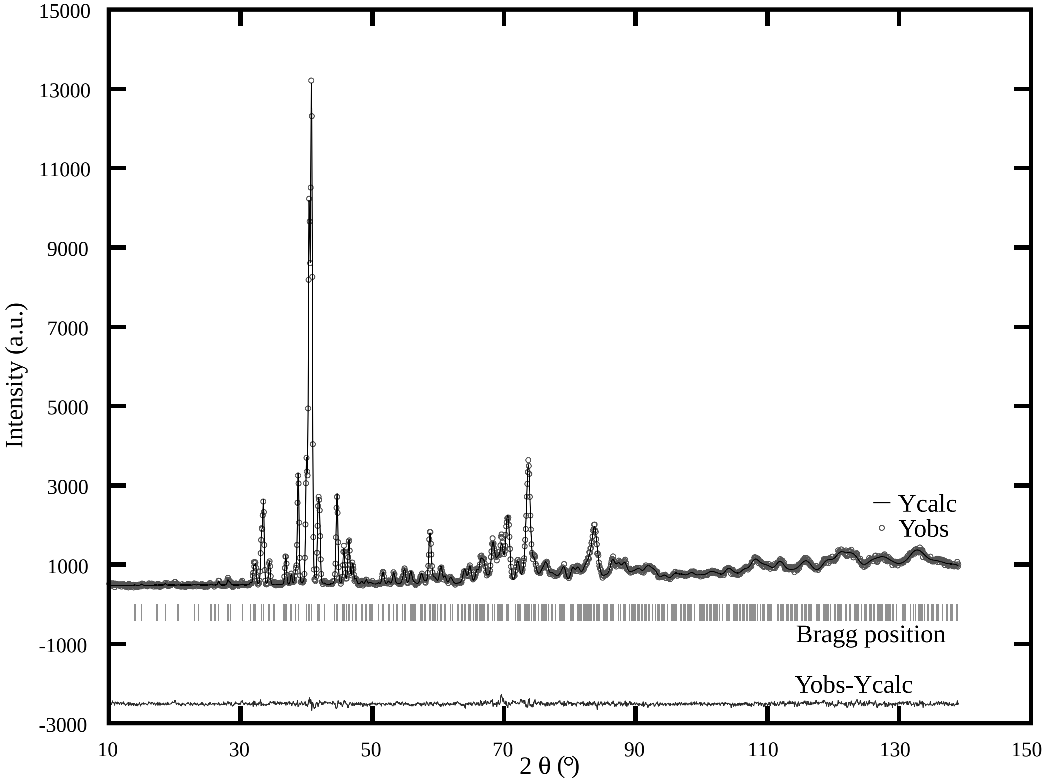

FIG. 1. Observed diffraction pattern, the calculated pattern and the difference curve for the neutron powder diffraction Rietveld refinement.

refinement strongly indicated that the cobalt atoms fully occupy one 6*c* position and partly occupy one 3*a* position. This gives in total 7.3(3) cobalt atoms (12.2(5) at% Co) in the unit cell, which agrees very well with the synthesis composition, 12.1 at% Co. It agrees reasonably well with the composition of the neutron diffraction powder sample that was 14 ± 3 at% Co from EDX.

TABLE 3
Coordinates and Thermal Parameters for δ-Co_2Zn_{15}, as Refined from the Neutron Powder Diffraction Data

Atom	Occ.	*x*	*y*	*z*	*B*
Co_1	1	0.421(2)	0.133(2)	0.23285	0.1(2)
Co_2	0.42(6)	0	0	0.246(6)	0.1(2)
Zn_2	0.58	0	0	0.246	0.58(3)
Zn_3	1	0.4241(8)	0.1571(8)	− 0.103(4)	0.58(3)
Zn_4	1	0.4814(8)	0.3708(8)	0.101(5)	0.58(3)
Zn_5	1	0.2292(8)	0.1634(8)	0.085(4)	0.58(3)
Zn_6	1	0.1897(1)	− 0.0269(9)	0.396(5)	0.58(3)
Zn_7	1	0.6608(8)	0.2781(8)	0.074(4)	0.58(3)
Zn_8	1	0.4260(8)	0.1120(7)	0.570(4)	0.58(3)
Zn_9	1	0.2425(7)	− 0.0713(7)	0.074(4)	0.58(3)
Zn_{10}	1	0.6259(9)	0.1102(9)	0.369(5)	0.58(3)
Zn_{11}	1	0.5	0	0.070(5)	0.58(3)

RESULTS AND DISCUSSION

The compound δ-Co_2Zn_{15} crystallizes in the acentric space group $P6_2$. The hexagonal unit cell contains 60 atoms (Pearson symbol *hP*60), of which 7.3 are Co. The compound is not stoichiometric, but the formula Co_2Zn_{15} gives a close approximation to the composition 12.1 at% Co corresponding to the formula $Co_{2.06}Zn_{15}$. The structure is best understood by considering the coordination polyhedra around the cobalt atom in 6*c* (Co_1). These are highly regular icosahedra of zinc (Zn_3–Zn_{11}) that share vertices to form a double helix around the translation hexad (Fig. 2a). The two helices are identical but are drawn in different shades of gray, to emphasize the double-helical structure. The inside of the helices forms a succession of distorted Archimedean antiprisms that are centered by a mixed occupancy 3c position (Co_2/Zn_2). The shared icosahedra vertices may also be taken as centers of icosahedra that share faces to form a regular icosahedra helix as defined by Lidin and Andersson (1). These helices are shown in Fig. 2b. Together, the two sets of helices form continuous icosahedral tubes that wrap around a hub of Archimedean antiprisms as shown in Fig. 2c. Such entities are packed in a simple hexagonal arrangement parallel to the hexagonal cell axis to make up the entire structure, as shown in Fig. 3c. It should

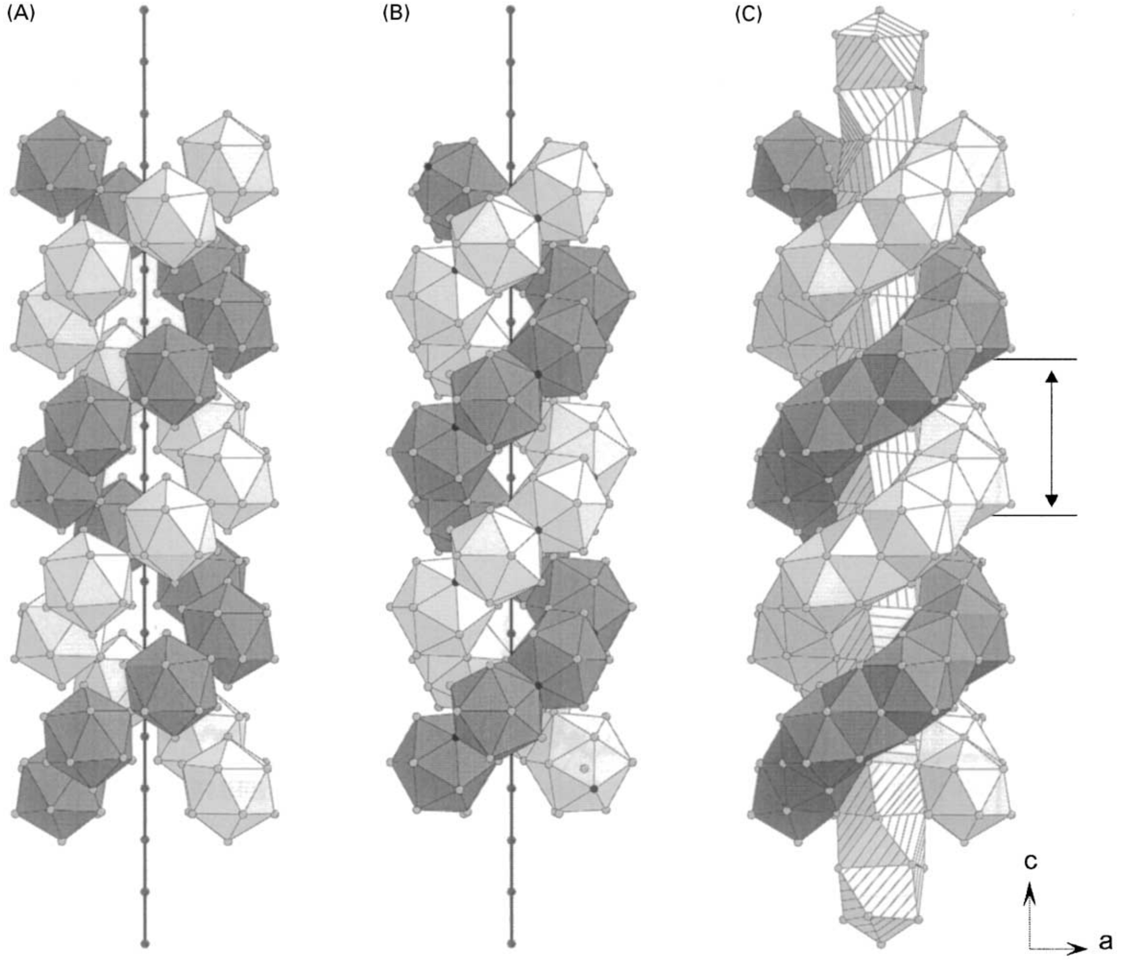

FIG. 2. (a) Double helix of vertex-sharing Co-centered icosahedra in δ-Co_2Zn_{15}. (b) Face-sharing icosahedra that interpenetrate the face-sharing icosahedra helix. (c) Full ensemble of helical cylinders of icosahedra that wrap around the hub of Archimedean antiprisms. The unit-cell repeat is indicated with arrows. The fully occupied cobalt atoms are drawn black and the mixed occupancy cobalt/zinc atoms are drawn dark gray.

be noted that this way of describing the structure is a very natural choice, since the helix is fully defined by the coordination polyhedra around the fully occupied heteroatom Co_1. The structure of δ-Co_2Zn_{15} is quite unique; indeed it seems to be the first intermetallic compound to crystallize in the space group $P6_2$. Chiral structures are fairly rare in intermetallics. Well-known examples include the Mg_2Ni type in space group $P6_222$ (12), Ir_3Zr_5 in $P6_122$ (13) and $RuZn_6$ (14) in $P4_132$. While icosahedral arrangements in zinc-rich intermetallics abound, the local arrangements of the icosahedra is unique in δ-Co_2Zn_{15}. Although the distinction is somewhat arbitrary, it is possible to divide the zinc-rich intermetallics into two groups; polar and nonpolar. In the more polar intermetallics, zinc atoms often form extended icosahedral networks containing large voids as in $NaZn_{13}$, $ScZn_{12}$ ($ThMn_{12}$-type) or $ThZn_{17}$. In the less polar compounds formed between Zn and late transition metals, it is still often possible to identify local icosahedral arrangements, but in these structures, the distinction between the elements is less pronounced, and the icosahedra interpenetrate, leading to several possible modes of description. This ambiguity of description is of course not limited to any particular set of structures, but rather a reflection of the fact that any structural description is a filter that permits us to understand the structure in a particular context. The description will highlight certain features and downplay others. Tetrahedrally close-packed structures (such as many of the zinc-rich late-transition-metal intermetallics) are extra difficult to rationalize since bonding patterns and valences are ill-defined, and thus natural building blocks are lacking. Still it may be noted that zinc along with other small metallic elements (Be, Al) tends to be icosagenic in its intermetallic chemistry, and that this may be attributed to the largely covalent nature of Zn–Zn interactions in such compounds.

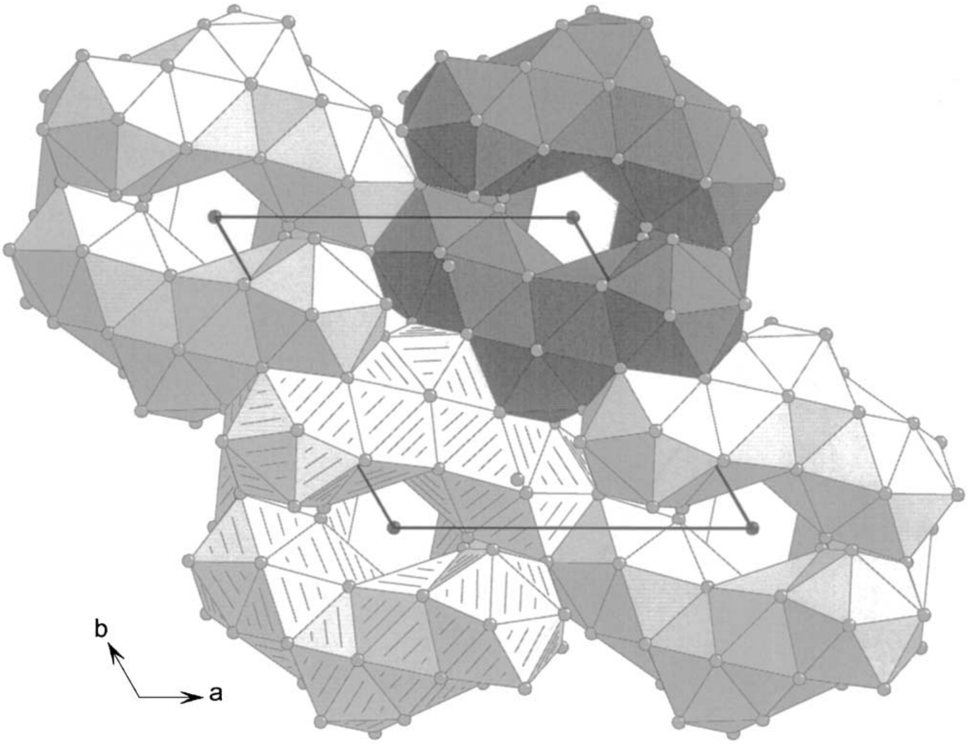

FIG. 3. Packing of double-helix cylinders in the hexagonal cell. The Archimedean antiprisms have been omitted for clarity. The patterns and shadings are made only to improve the visualization. The Co_2/Zn_2 atoms at $0\,0\,z$ which have mixed cobalt/zinc occupancy are drawn dark gray.

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