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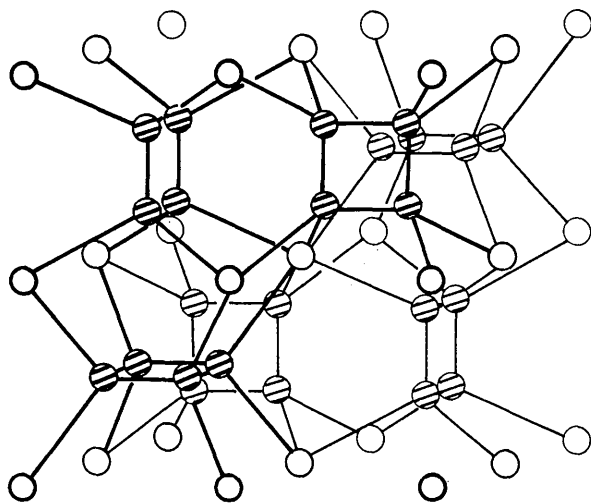
The refinement of the crystal structure of skutterudite, CoAs₃. By NEIL MANDEL and JERRY DONOHUE, *Department of Chemistry and Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19104, U.S.A.*

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The crystal structure of skutterudite, cobalt triarsenide, has been re-refined with new data collected at 22°C on a Picker automatic diffractometer (Mo K α) out to a maximum $\sin \theta/\lambda = 0.60$, with the moving-crystal moving-counter technique. There were 224 unique reflections collected. Space group is $Im\bar{3} (T_h^5)$ with eight formulas per unit cell, with $a = 8.195 \pm 0.003$ Å. Each cobalt atom is surrounded octahedrally by six arsenic neighbors at a distance of 2.334 ± 0.001 Å. The arsenic atoms form rectangles with bond distances of 2.464 ± 0.002 and 2.572 ± 0.002 Å. Final R is 3.5%.

The refinement of the structure of skutterudite, CoAs₃, was undertaken to study the four-membered arsenic ring structure. A view of this structure is shown in Fig. 1. The structures of skutterudite-type phosphides have been studied by Rundqvist & Ersson (1968) who showed that the cobalt atoms have a trigonally distorted octahedral environment of six phosphorus atoms. The phosphorus atoms form rectangles in preference to squares which had been postulated by Oftedal (1928) in the original determination of the skutterudite structure. The single-crystal study on skutterudite by Ventriglia (1957) was the first to indicate a distorted cobalt octahedron and rectangles of arsenic atoms.

The crystal used in the present investigation was a truncated octahedron (0.23 mm average diameter) chipped from an ore sample from Bou-Azzer, Morocco. From elemental analysis the sample of skutterudite contained 67.5% As, 15.7% Co, 2.1% Fe, 2.6% Ni, and trace amounts of Ir, Pd, Rh, and Sb. This corresponds to the formula $Co_{0.87}Fe_{0.11}Ni_{0.13}As_{3.0}$. Some oxide was doubtless present, as well as some silicate matrix. The linear absorption coefficient is 447.6 cm^{-1} , and due to the almost spherical nature of the crystal, a simple spherical absorption correction was applied to the data using the transmission factors from *International Tables for X-ray Crystallography* (1967). The space group was verified as $Im\bar{3} (T_h^5)$ from



Co ○ As ⊙

Fig. 1. One unit cell of the skutterudite structure.

Table 1. Observed and calculated structure factors
Unobserved factors are designated by asterisks.

hkl	F _o	F _c	hkl	F _o	F _c	hkl	F _o	F _c	hkl	F _o	F _c
-4 2 3	73.1	73.1	-5 3 6	114.5	117.3	-2 2 0	77.0	81.8	-1 1 4	57.1	58.4
-4 2 1	96.7	98.8	-5 3 4	121.1	122.9	-2 2 8	150.1	152.9	-1 1 2	101.2	104.1
-4 2 5	142.6	143.5	-5 3 2	127.8	128.8	-2 2 4	176.0	176.0	-1 1 0	121.1	125.4
-4 2 7	182.1	182.8	-5 3 0	132.8	135.4	-2 2 8	176.0	176.0	-1 2 5	113.9	7.5
-4 2 9	205.5	212.1	-5 3 4	139.1	142.9	-2 2 4	198.7	198.7	-1 2 3	137.2	84.8
-4 2 11	224.2	231.0	-5 3 6	144.1	148.9	-2 2 0	211.0	211.0	-1 2 1	158.5	205.8
-4 2 13	238.2	247.0	-5 3 8	148.1	153.9	-2 2 4	223.0	223.0	-1 2 0	178.8	205.8
-4 2 15	248.2	257.7	-5 3 10	151.1	157.1	-2 2 8	235.0	235.0	-1 2 8	207.8	205.8
-4 2 17	254.9	264.5	-5 3 12	153.1	159.1	-2 2 4	247.0	247.0	-1 2 6	221.8	211.8
-4 2 19	259.2	269.2	-5 3 14	154.1	161.1	-2 2 0	259.0	259.0	-1 2 4	235.8	225.8
-4 2 21	262.1	272.1	-5 3 16	155.1	163.1	-2 2 4	271.0	271.0	-1 2 2	249.8	241.8
-4 2 23	263.8	273.8	-5 3 18	155.1	165.1	-2 2 8	283.0	283.0	-1 2 0	263.8	253.8
-4 2 25	264.2	274.2	-5 3 20	155.1	167.1	-2 2 4	295.0	295.0	-1 2 8	277.8	267.8
-4 2 27	263.5	273.5	-5 3 22	154.1	169.1	-2 2 0	307.0	307.0	-1 2 6	291.8	281.8
-4 2 29	261.5	271.5	-5 3 24	153.1	171.1	-2 2 4	319.0	319.0	-1 2 4	305.8	295.8
-4 2 31	258.2	268.2	-5 3 26	151.1	173.1	-2 2 8	331.0	331.0	-1 2 2	319.8	309.8
-4 2 33	253.7	263.7	-5 3 28	148.1	175.1	-2 2 4	343.0	343.0	-1 2 0	333.8	323.8
-4 2 35	248.2	258.2	-5 3 30	144.1	177.1	-2 2 0	355.0	355.0	-1 2 8	347.8	337.8
-4 2 37	241.7	251.7	-5 3 32	139.1	179.1	-2 2 4	367.0	367.0	-1 2 6	361.8	351.8
-4 2 39	234.2	244.2	-5 3 34	133.1	181.1	-2 2 8	379.0	379.0	-1 2 4	375.8	365.8
-4 2 41	225.7	235.7	-5 3 36	126.1	183.1	-2 2 4	391.0	391.0	-1 2 2	389.8	379.8
-4 2 43	216.2	226.2	-5 3 38	119.1	185.1	-2 2 0	403.0	403.0	-1 2 0	403.8	393.8
-4 2 45	205.7	215.7	-5 3 40	111.1	187.1	-2 2 4	415.0	415.0	-1 2 8	417.8	407.8
-4 2 47	194.2	204.2	-5 3 42	102.1	189.1	-2 2 8	427.0	427.0	-1 2 6	431.8	421.8
-4 2 49	181.7	191.7	-5 3 44	92.1	191.1	-2 2 4	439.0	439.0	-1 2 4	445.8	435.8
-4 2 51	168.2	178.2	-5 3 46	81.1	193.1	-2 2 0	451.0	451.0	-1 2 2	459.8	449.8
-4 2 53	153.7	163.7	-5 3 48	69.1	195.1	-2 2 4	463.0	463.0	-1 2 0	473.8	463.8
-4 2 55	138.2	148.2	-5 3 50	56.1	197.1	-2 2 8	475.0	475.0	-1 2 8	487.8	477.8
-4 2 57	121.7	132.7	-5 3 52	42.1	199.1	-2 2 4	487.0	487.0	-1 2 6	501.8	491.8
-4 2 59	104.2	116.2	-5 3 54	27.1	201.1	-2 2 0	499.0	499.0	-1 2 4	515.8	505.8
-4 2 61	85.7	97.7	-5 3 56	11.1	203.1	-2 2 4	511.0	511.0	-1 2 2	529.8	519.8
-4 2 63	66.2	78.2	-5 3 58	-5.1	205.1	-2 2 8	523.0	523.0	-1 2 0	543.8	533.8
-4 2 65	45.7	57.7	-5 3 60	-19.1	207.1	-2 2 4	535.0	535.0	-1 2 8	557.8	547.8
-4 2 67	24.2	36.2	-5 3 62	-33.1	209.1	-2 2 0	547.0	547.0	-1 2 6	571.8	561.8
-4 2 69	2.7	14.7	-5 3 64	-47.1	211.1	-2 2 4	559.0	559.0	-1 2 4	585.8	575.8
-4 2 71	* * *	* * *	-5 3 66	-61.1	213.1	-2 2 8	571.0	571.0	-1 2 2	599.8	589.8
-4 2 73	* * *	* * *	-5 3 68	-75.1	215.1	-2 2 4	583.0	583.0	-1 2 0	613.8	603.8
-4 2 75	* * *	* * *	-5 3 70	-89.1	217.1	-2 2 0	595.0	595.0	-1 2 8	627.8	617.8
-4 2 77	* * *	* * *	-5 3 72	-103.1	219.1	-2 2 4	607.0	607.0	-1 2 6	641.8	631.8
-4 2 79	* * *	* * *	-5 3 74	-117.1	221.1	-2 2 8	619.0	619.0	-1 2 4	655.8	645.8
-4 2 81	* * *	* * *	-5 3 76	-131.1	223.1	-2 2 4	631.0	631.0	-1 2 2	669.8	659.8
-4 2 83	* * *	* * *	-5 3 78	-145.1	225.1	-2 2 0	643.0	643.0	-1 2 0	683.8	673.8
-4 2 85	* * *	* * *	-5 3 80	-159.1	227.1	-2 2 4	655.0	655.0	-1 2 8	697.8	687.8
-4 2 87	* * *	* * *	-5 3 82	-173.1	229.1	-2 2 8	667.0	667.0	-1 2 6	711.8	701.8
-4 2 89	* * *	* * *	-5 3 84	-187.1	231.1	-2 2 4	679.0	679.0	-1 2 4	725.8	715.8
-4 2 91	* * *	* * *	-5 3 86	-201.1	233.1	-2 2 0	691.0	691.0	-1 2 2	739.8	729.8
-4 2 93	* * *	* * *	-5 3 88	-215.1	235.1	-2 2 4	703.0	703.0	-1 2 0	753.8	743.8
-4 2 95	* * *	* * *	-5 3 90	-229.1	237.1	-2 2 8	715.0	715.0	-1 2 8	767.8	757.8
-4 2 97	* * *	* * *	-5 3 92	-243.1	239.1	-2 2 4	727.0	727.0	-1 2 6	781.8	771.8
-4 2 99	* * *	* * *	-5 3 94	-257.1	241.1	-2 2 0	739.0	739.0	-1 2 4	795.8	785.8
-4 2 101	* * *	* * *	-5 3 96	-271.1	243.1	-2 2 4	751.0	751.0	-1 2 2	809.8	799.8
-4 2 103	* * *	* * *	-5 3 98	-285.1	245.1	-2 2 8	763.0	763.0	-1 2 0	823.8	813.8
-4 2 105	* * *	* * *	-5 3 100	-299.1	247.1	-2 2 4	775.0	775.0	-1 2 8	837.8	827.8
-4 2 107	* * *	* * *	-5 3 102	-313.1	249.1	-2 2 0	787.0	787.0	-1 2 6	851.8	841.8
-4 2 109	* * *	* * *	-5 3 104	-327.1	251.1	-2 2 4	799.0	799.0	-1 2 4	865.8	855.8
-4 2 111	* * *	* * *	-5 3 106	-341.1	253.1	-2 2 8	811.0	811.0	-1 2 2	879.8	869.8
-4 2 113	* * *	* * *	-5 3 108	-355.1	255.1	-2 2 4	823.0	823.0	-1 2 0	893.8	883.8
-4 2 115	* * *	* * *	-5 3 110	-369.1	257.1	-2 2 0	835.0	835.0	-1 2 8	907.8	897.8
-4 2 117	* * *	* * *	-5 3 112	-383.1	259.1	-2 2 4	847.0	847.0	-1 2 6	921.8	911.8
-4 2 119	* * *	* * *	-5 3 114	-397.1	261.1	-2 2 8	859.0	859.0	-1 2 4	935.8	925.8
-4 2 121	* * *	* * *	-5 3 116	-411.1	263.1	-2 2 4	871.0	871.0	-1 2 2	949.8	939.8
-4 2 123	* * *	* * *	-5 3 118	-425.1	265.1	-2 2 0	883.0	883.0	-1 2 0	963.8	953.8
-4 2 125	* * *	* * *	-5 3 120	-439.1	267.1	-2 2 4	895.0	895.0	-1 2 8	977.8	967.8
-4 2 127	* * *	* * *	-5 3 122	-453.1	269.1	-2 2 8	907.0	907.0	-1 2 6	991.8	981.8
-4 2 129	* * *	* * *	-5 3 124	-467.1	271.1	-2 2 4	919.0	919.0	-1 2 4	1005.8	995.8
-4 2 131	* * *	* * *	-5 3 126	-481.1	273.1	-2 2 0	931.0	931.0	-1 2 2	1019.8	1009.8
-4 2 133	* * *	* * *	-5 3 128	-495.1	275.1	-2 2 4	943.0	943.0	-1 2 0	1033.8	1023.8
-4 2 135	* * *	* * *	-5 3 130	-509.1	277.1	-2 2 8	955.0	955.0	-1 2 8	1047.8	1037.8
-4 2 137	* * *	* * *	-5 3 132	-523.1	279.1	-2 2 4	967.0	967.0	-1 2 6	1061.8	1051.8
-4 2 139	* * *	* * *	-5 3 134	-537.1	281.1	-2 2 0	979.0	979.0	-1 2 4	1075.8	1065.8
-4 2 141	* * *	* * *	-5 3 136	-551.1	283.1	-2 2 4	991.0	991.0	-1 2 2	1089.8	1079.8
-4 2 143	* * *	* * *	-5 3 138	-565.1	285.1	-2 2 8	1003.0	1003.0	-1 2 0	1103.8	1093.8
-4 2 145	* * *	* * *	-5 3 140	-579.1	287.1	-2 2 4	1015.0	1015.0	-1 2 8	1117.8	1107.8
-4 2 147	* * *	* * *	-5 3 142	-593.1	289.1	-2 2 0	1027.0	1027.0	-1 2 6	1131.8	1121.8
-4 2 149	* * *	* * *	-5 3 144	-607.1	291.1	-2 2 4	1039.0	1039.0	-1 2 4	1145.8	1135.8
-4 2 151	* * *	* * *	-5 3 146	-621.1	293.1	-2 2 8	1051.0	1051.0	-1 2 2	1159.8	1149.8
-4 2 153	* * *	* * *	-5 3 148	-635.1	295.1	-2 2 4	1063.0	1063.0	-1 2 0	1173.8	1163.8
-4 2 155	* * *	* * *	-5 3 150	-649.1	297.1	-2 2 0	1075.0	1075.0	-1 2 8	1187.8	1177.8
-4 2 157	* * *	* * *	-5 3 152	-663.1	299.1	-2 2 4	1087.0	1087.0	-1 2 6	1201.8	1191.8
-4 2 159	* * *	* * *	-5 3 154	-677.1	301.1	-2 2 8	1099.0	1099.0	-1 2 4	1215.8	1205.8
-4 2 161	* * *	* * *	-5 3 156	-691.1	303.1	-2 2 4	1111.0	1111.0	-1 2 2	1229.8	1219.8
-4 2 163	* * *	* * *	-5 3 158	-705.1	305.1	-2 2 0	1123.0	1123.0	-1 2 0	1243.8	1233.8
-4 2 165	* * *	* * *	-5 3 160	-719.1	307.1	-2 2 4	1135.0	1135.0	-1 2 8	1257.8	1247.8
-4 2 167	* * *	* * *	-5 3 162	-733.1	309.1	-2 2 8	1147.0	1147.0	-1 2 6	1271.8	1261.8
-4 2 169	* * *	* * *	-5 3 164	-747.1	311.1	-2 2 4	1159.0	1159.0	-1 2 4	1285.8	1275.8
-4 2 171	* * *	* * *	-5 3 166	-761.1	313.1	-2 2 0	1171.0	1171.0	-1 2 2	1299.8	1289.8
-4 2 173	* * *	* * *	-5 3 168	-775.1	315.1	-2 2 4	1183.0	1183.0	-1 2 0	1313.8	1303.8
-4 2 175	* * *	* * *	-5 3 170	-789.1	317.1	-2 2 8	1195.0	1195.0	-1 2 8	1327.8	1317.8
-4 2 177	* * *	* * *	-5 3 172	-803.1	319.1	-2 2 4	1207.0	1207.0</			

Table 2. Final positional and thermal parameters with e.s.d.'s (all $\times 10^4$)

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co	($\frac{1}{4}$)	($\frac{1}{4}$)	($\frac{1}{4}$)	45 (2)	($=\beta_{11}$)	($=\beta_{11}$)	4 (4)	($=\beta_{12}$)	($=\beta_{12}$)
As	(0)	3431 (1)	1503 (1)	27 (1)	35 (1)	32 (1)	(0)	(0)	2 (3)

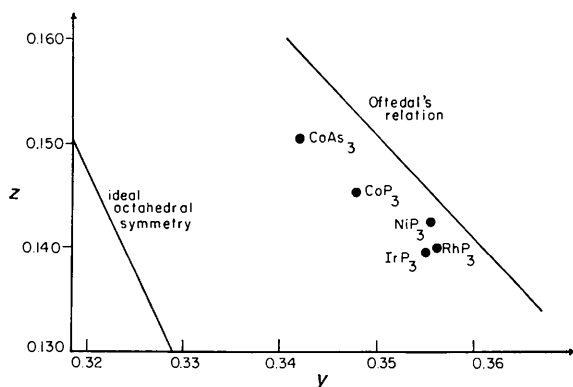


Fig. 2. Oftedal's relation versus ideal octahedral symmetry, with phosphide structures from Rundqvist & Ersson (1968).

Three quantities are of particular interest in discussing the structure: the Co-As distance, the distortion of the As_4 groups from a square, and the degree of distortion of the $CoAs_6$ octahedron. For the two As-As distances equal, $2(y+z)=1$. This trival equation has been called the Oftedal relation. For regular octahedral coordination about the Co atom, the parameters y and z for the As atoms must satisfy the relation $y(2z-1)=z-\frac{1}{2}$. Deviation from this relationship leads to a trigonal antiprismatic distortion from octahedral symmetry. The distances for the Oftedal structure are Co-As = 2.35 Å, and As-As = 2.45 Å. Ventriglia's distances are Co-As = 2.23 Å, As-As = 2.55 and 4.09 Å. Ventriglia stated that these distances agreed better with experimental data, but gave no observed or calculated structure factors. The distances found in the present study are Co-As = 2.334 ± 0.001 Å, As-As = 2.572 ± 0.002 and 2.464 ± 0.002 Å. The two As-Co-As angles in the octahedron are 95.4 and 84.6°. Fig. 2 shows the relation between y and z for regular octahedral coordination and for equal As-As distances. Note, as was also pointed out by Rundqvist & Ersson (1968), that both 'ideal' conditions cannot be realized simultaneously without a change in the structure type, as mentioned below.

Following the discussion of Rundqvist & Ersson (1968), an increasing trigonal distortion of the ideal octahedral symmetry of the ligands about the Co atoms presumably

leads to a less favorable energetic situation as regards the Co-As bonds. On the other hand, a departure from the Oftedal relation, which means an elongation of two of the As-As bonds, probably leads to a less favorable bonding in the As_4 rings. As seen in Fig. 2, Oftedal's relation and the condition for ideal octahedral symmetry cannot be simultaneously fulfilled, except for a drastic structural change to the ReO_3 -type structure. This condition occurs at the intersection of the extension of the two lines in Fig. 2, at $y=z=\frac{1}{4}$. Since the presence of As-As bonding is apparently essential for the stability of the compounds, a compromise is reached between the two opposing factors.

Note that in the skutterudite-type phosphides, the shorter P-P bond distance is virtually constant at 2.23 ± 0.01 Å which corresponds well with the P-P distances of 2.21 Å in P_4 and 2.25 Å in P_4S_3 (Sutton, 1958). In skutterudite itself the shorter As-As distance of 2.46 Å is in good agreement with distances of 2.45 Å in $(AsCF_3)_4$ (Mandel & Donohue, 1971), 2.43 Å in $(AsCH_3)_5$ (Burns & Waser, 1957), 2.46 Å in $(AsC_6H_5)_6$ (Hedberg, Hughes & Waser, 1961), and of 2.44 Å in gaseous As_4 (Maxwell, Hendricks & Moseley, 1935).

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A simple 'direct' solution of the crystallographic phase problem. By A. L. MACDONALD, J. M. ROBERTSON and J. C. SPEAKMAN, *Chemistry Department, The University, Glasgow W.2, Scotland*

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The 'difference' Patterson function, based on neutron-diffraction data, between a hydrogen compound and its deuteriate led to a direct, and absolute, structure determination.

We have recently completed precise structure analyses of potassium hydrogen di-trifluoroacetate, $KH(CF_3CO_2)_2$, and

its deuteriate, $KD(CF_3CO_2)_2$, based on full neutron-diffraction data (Macdonald & Speakman, 1971). We then com-