Table 2. Interatomic distances in V_2P (Å units). Distances shorter than 3.5 Å are listed. The estimated standard deviations are smaller than 0.001 Å for all distances.

$V(1)-2P$	2.341	$V(2)-2P$	2.461
— P	2.366	— 2P	2.547
— P	2.474	— P	2.674
— 2V(1)	2.545	— 2V(1)	2.716
— 2V(2)	2.716	— 2V(1)	2.872
— 2V(2)	2.872	— V(1)	3.013
— V(2)	3.013	— V(1)	3.025
— V(2)	3.025	— 2V(2)	3.043
— 2V(1)	3.305	— 2V(2)	3.305
		— 2V(2)	3.349
P — 2P	3.305		

single-crystal analysis showed that V_2P is indeed a new member of this class.

It is interesting to compare the atomic arrangement of V_2P with that of the isotypic Ru_2P ,⁷ since the metal radii are approximately equal. Different arrangements are found, which implies that the radius ratio is not the governing factor. The b -axis of Ru_2P is 3.859 Å while that of V_2P is only 3.305 Å. Thus the trigonal prisms in V_2P are contracted compared to those in Ru_2P , which demand the metal atoms outside the prism faces to be positioned further away from the central phosphorus atom. These M—P distances are then longer while within the prisms the M—P distances as well as the M—M distances are shorter than in Ru_2P . This leads to a more even distribution of the M—P distances but a larger spread of the M—M distances in V_2P . These geometrical aspects were introduced and thoroughly discussed by Rundqvist.¹² The interatomic distances in V_2P are presented in Table 2, using the same notation as Rundqvist. The mean $V(1)$ —P distance is 2.38 Å and the mean $Ru(1)$ —P distance is 2.34 Å. Corresponding averages for the $M(2)$ —P distances are 2.54 and 2.61 Å for V_2P and Ru_2P , respectively. The shortest M—M distance in Ru_2P is 2.74 Å as compared to 2.55 Å in V_2P , the latter distance being shorter than a normal metal contact. Short intermetallic distances are not uncommon in vanadium-rich compounds with Group 4 or 5 elements.

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1. Berger, R. *Acta Chem. Scand. A* 29 (1975) 641.
2. Boller, H. *Monatsh. Chem.* 104 (1973) 48.
3. Andrew, T. R. *Analyst* 82 (1957) 423.

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4. Gustafsson, L. University of Uppsala. *Private communication*.
5. Deslattes, R. D. and Henins, A. *Phys. Rev. Lett.* 31 (1973) 972.
6. Lundgren, J.-O., Ed., *Crystallographic Computer Programs*, Institute of Chemistry, University of Uppsala, Uppsala 1975, UUIC-B13-04-2.
7. Rundqvist, S. *Acta Chem. Scand.* 14 (1960) 1961.
8. Hanson, H. P., Herman, F., Lea, J. D. and Skillman, S. *Acta Crystallogr.* 17 (1964) 1040.
9. Cromer, D. T. *Acta Crystallogr.* 18 (1965) 17.
10. Hirshfeld, F. L. and Rabinovich, D. *Acta Crystallogr. A* 29 (1973) 510.
11. Rundqvist, S. *Acta Chem. Scand.* 15 (1961) 342.
12. Rundqvist, S. *Ark. Kemi* 20 (1962) 67.
13. Shoemaker, C. B. and Shoemaker, D. P. *Acta Crystallogr.* 18 (1965) 900.

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On the Compound $La_4Co_3O_{10}$

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Some binary oxides, of general formulae AO and BO_2 , form ternary compounds $AO(ABO_3)_n$, where one at the one end finds the perovskite ABO_3 ($n=\infty$) type structure and at the other the A_2BO_4 ($n=1$) the K_2NiF_4 type. Two further members of a series are known, viz. $A_2B_2O_7$ ($n=2$) and $A_4B_3O_{10}$ ($n=3$), but none has reported examples for n between 3 and ∞ . The structure of $AO(ABO_3)_n$ contains n perovskite sheets separated by an AO sheet of NaCl like structure. Such series are known in the systems $CaO-MnO_2$, $CaO-TiO_2$, $SrO-MnO_2$, $SrO-TiO_2$, and $SrO-ZrO_2$.¹

In the system $La-Co-O$ $LaCoO_3$ and La_2CoO_4 with rhombohedrally modified perovskite and orthorhombic K_2NiF_4 type structures^{2,3} are known. We have prepared $La_4Co_3O_{10}$,⁴ which also has been reported quite recently by Janecek and Wirtz.⁵

Experimental. Initial batches of $LaCoO_3$ and La_2CoO_4 were prepared from 99.99 % La_2O_3 (Kemira OY) and 99.95 % CoO (Sheritt Gordon). Powder mixtures were coldpressed at 9.8 kN/cm². $LaCoO_3$ -specimens were fired for one week at 1100 °C in oxygen atmosphere and La_2CoO_4 -tablets for four days at 1300 °C in argon ($PO_2 \approx 10^{-6}$ bar) with frequent inter-

Table 1. X-Ray powder data of $\text{La}_4\text{Co}_3\text{O}_{10}$.

d_o	d_c	hkl	I_o	d_c	d_c	hkl	I_o
3.816	3.814	111	16	1.712	1.712	311	2
3.560	3.557	113	5	1.688	1.687	313	2
3.480	3.476	008	10	1.684	1.684	228	4
3.171	3.166	115	3	1.670	1.670	11 15	10
2.763	2.765	117	100	1.607	1.607	02 14	
2.734	2.735	020	32	1.602	1.602	20 14	10
2.710	2.710	200	32	1.586	1.585	137	
2.410	2.410	119	7	1.583	1.583	22 10	35
	2.356	026		1.574	1.575	317	9
2.348			3				
	2.340	206		1.509	1.508	139	2
2.148	2.149	028	19		1.506	11 17	
				1.503			1
2.137	2.137	208	10		1.500	319	
2.114	2.113	11 11	3	1.467	1.467	02 16	6
	1.950	02 10		1.464	1.463	20 16	
1.946			3				
	1.941	20 10		1.382	1.382	22 14	11
1.925	1.925	220	38	1.368	1.368	11 19	4
1.738	1.738	00 16	3	1.355	1.355	400	4
1.725	1.725	131	2	1.345	1.345	02 18	1

mediate grindings. $\text{La}_4\text{Co}_3\text{O}_{10}$ -specimens were finally prepared from LaCoO_3 and La_2CoO_4 powders kept at 1130°C in nitrogen atmosphere ($p\text{O}_2 = 10^{-3.55}$ bar) for five days.

The powder pattern of $\text{La}_4\text{Co}_3\text{O}_{10}$ was run by X-ray diffractometer PW 1410/20 using graphite monochromatized $\text{CuK}\alpha$ -radiation ($\lambda = 1.5418 \text{ \AA}$) at a scanning speed of $0.25^\circ/\text{min}$ and a silicon powder ($a = 5.4301 \text{ \AA}$) as an internal standard.

The powder pattern of $\text{La}_4\text{Co}_3\text{O}_{10}$ was satisfactorily indexed with orthorhombic unit cell parameters, $a = 5.42 \text{ \AA}$, $b = 5.47 \text{ \AA}$ and $c = 27.81 \text{ \AA}$. The measured density, 7.1 g cm^{-3} , corresponds to four formula units per cell ($D_x = 7.21 \text{ g cm}^{-3}$). All indexes are unmixed, Table 1, so a possible space group is $Fmmm$ (No. 69).

In our investigation of the $\text{La}-\text{Co}-\text{O}$ -system we have obtained no evidence for $\text{La}_3\text{Co}_2\text{O}_7$. We shall later report on thermodynamic investigations of the system $\text{La}-\text{Co}-\text{O}$ and also the powder pattern of $\text{La}_4\text{Ni}_3\text{O}_{10}$.

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- Goodenough, J. B. and Longo, J. *Landolt-Börnstein Tabellen* Neue Serie III/4a, p. 203, Springer (Berlin) 1970.

- Rabenau, A. and Eckerlin, P. *Acta Crystallogr.* 11 (1958) 304.
- Lehuede, P. and Daire, M. *C. R. Acad. Sci.* 276 (1973) 1783.
- Tikkanen, M. H. and Seppänen, M. *Research Report for the Academy of Finland*, Part 1, Febr. 1975.
- Janecek, J. J., Wirtz, G. P. *Am. Ceram. Soc. Bull.* 54 (1975) 739.

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