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The Refinement of the Crystal Structure of Potassium Caprate (Form *A*)

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Form *A* of the soap potassium caprate, $CH_3(CH_2)_8COOK$, is monoclinic with $a=8·03\pm0·02$, $b=5·69\pm0·02$, $c=28·04\pm0·07$ Å, $\beta=100·2\pm0·2°$. The space group is $P2_1/a$ with four molecules per unit cell. The hydrocarbon chains are packed in a crossed-chain structure with an angle of tilt of $57·9\pm0·5°$. Very large, anisotropic, thermal motions of the four carbon atoms nearest the methyl group ends of the chains are reported. These four atoms are those which alter their positions in the transition to the *C* phase which occurs at 76°C.

Introduction

The crystal structures of the anhydrous soaps with monovalent cations are of special interest because the crystal structures taken up depend on the interplay of ionic forces which act between the cations and the polar groups of the fatty acid radicals, and molecular forces which act between neighbouring hydrocarbon chains. The structure that occurs in practice depends on the nature of the cation, the chain length, the temperature, the degree of hydration and, in some cases, on the method of preparation. Because good single crystals of anhydrous sodium soaps are difficult to prepare, previous work on the crystallography of anhydrous soaps has tended to concentrate on the structure of potassium soaps.

Piper (1929) reported one form each of the neutral and 1:1 acid potassium soaps, and Vand, Lomer & Lang (1947) established the existence of three anhydrous forms, *A*, *B* and *C*, of neutral potassium soaps containing an even number of carbon atoms in the chain. Form *A* is monoclinic and occurs when soaps containing from four to ten carbon atoms are crystallized from alcohol at room temperature; form *B*, which

Table 1. *Atom parameters: coordinates as fractions of the unit cell; vibration tensor components in* Å²

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{13}$	$2U_{12}$
K	0·39049	0·25151	0·03852	0·0470	0·0381	0·0657	−0·0016	0·0303	−0·0032
O(1)	0·15539	0·55906	0·05672	0·0737	0·0338	0·0725	0·0009	0·0469	0·0019
O(2)	0·15630	0·94968	0·05777	0·0682	0·0411	0·0863	0·0138	0·0366	−0·0089
C(1)	0·15206	0·75515	0·07820	0·0419	0·0346	0·0681	−0·0169	0·0183	−0·0056
C(2)	0·13777	0·74880	0·13248	0·0733	0·0317	0·0723	−0·0116	0·0393	−0·0210
C(3)	0·13726	0·50912	0·15582	0·0709	0·0863	0·0718	0·0025	0·0269	−0·0150
C(4)	0·13710	0·52474	0·21062	0·0737	0·1038	0·0659	0·0082	0·0284	0·0076
C(5)	0·13466	0·28273	0·23473	0·0863	0·0899	0·0731	0·0234	0·0532	0·0152
C(6)	0·12969	0·29349	0·28915	0·0895	0·1090	0·0696	0·0310	0·0317	0·0009
C(7)	0·12737	0·05971	0·31350	0·1008	0·1502	0·0715	0·0884	0·0408	−0·0088
C(8)	0·12250	0·07558	0·36873	0·1077	0·2049	0·0837	0·1094	0·0430	−0·0028
C(9)	0·11262	−0·15767	0·39193	0·1887	0·2504	0·0960	0·1029	0·0858	0·0008
C(10)	0·10635	−0·13611	0·44680	0·2398	0·3767	0·1093	0·1388	0·0945	−0·0081
				U_{iso}					
H(1)	0·235	0·875	0·1513	0·096					
H(2)	0·074	0·895	0·1372	0·233					
H(3)	0·265	0·396	0·1580	0·121					
H(4)	0·034	0·396	0·1393	0·014					
H(5)	0·235	0·611	0·2329	0·066					
H(6)	0·030	0·655	0·2181	0·139					
H(7)	0·228	0·155	0·2298	0·061					
H(8)	0·026	0·188	0·2170	0·062					
H(9)	0·233	0·401	0·3096	0·103					
H(10)	0·037	0·434	0·2916	0·072					
H(11)	0·237	−0·043	0·2916	0·069					
H(12)	0·023	−0·050	0·2966	0·114					
H(13)	0·242	0·158	0·3944	0·091					
H(14)	0·030	0·183	0·3757	0·131					
H(15)	0·223	−0·269	0·3910	0·243					
H(16)	0·024	−0·252	0·3740	0·205					
H(17)	0·232	−0·018	0·4638	0·185					
H(18)	0·002	−0·018	0·4485	0·240					
H(19)	0·077	−0·325	0·4603	0·249					

is identical with the form described by Piper, is triclinic and occurs under similar conditions to those for the longer chain length soaps, and form *C* results when either the *A* or *B* form is heated to higher temperatures. The crystal structure of form *B* has been reported by Dumbleton & Lomer (1965) and the approximate structure of form *A* has been described by Vand, Lomer & Lang (1949). (This work is referred to below as VLL.) The crystal used by VLL was observed to possess disorder which caused the 11*l* and 33*l* reflexions to be diffuse; Dumbleton (1964) attempted to refine the structure using the data of VLL and Curtis's (1959) least-squares refinement program, but the refinement failed. In order to confirm the structure of the *A* form it was decided to collect more diffraction data and to redetermine the structure.

Experimental

Potassium caprate was prepared by neutralizing a dilute alcoholic solution of pure n-capric acid with an alcoholic solution of potassium ethoxide using phenolphthalein as indicator. Some care was taken to exclude water from the solutions, since its presence prevented any good crystals being obtained; dilute solutions were used since more concentrated solutions caused a gel-like precipitate to form on titration. The neutral solution was evaporated slowly to dryness over anhydrous calcium chloride in an evacuated desiccator. The crystals obtained were flat colourless plates, usually with malformed edges, the large faces being (001). They were soft and easily damaged. Some of the crystals were found to be twinned on the large, (001), face and many possessed disorder such that reflexions with *h* odd were extended in reciprocal space along the **c*** direction. This type of diffuseness is due to a stacking fault, with a shift of $\frac{1}{2}a$, between molecular layers parallel to the (001) planes. This simple type of disorder is perhaps the only known example of the disorder discussed by Wilson (1962) and is similar to that suggested by VLL. The single crystals used for X-ray examination were about 0·8 × 0·5 × 0·04 mm, and showed no signs of disorder or twinning. Zero-layer and equiinclination upper layer Weissenberg photographs were taken with the crystal rotating about the *a* and *b* axes. The unit cell was found to be monoclinic with $a = 8{\cdot}03 \pm 0{\cdot}02$, $b = 5{\cdot}69 \pm 0{\cdot}02$, $c = 28{\cdot}04 \pm 0{\cdot}07$ Å and $\beta = 100{\cdot}2 \pm 0{\cdot}2°$; the long spacing ($= 1/c^*$) was $27{\cdot}60 \pm 0{\cdot}07$ Å, and assuming 4 molecules of $C_{10}H_{19}O_2K$ per unit cell the calculated density was $1{\cdot}108 \pm 0{\cdot}004$ g.cm^{-3} which agreed satisfactorily with the observed value of $1{\cdot}123 \pm 0{\cdot}005$ g.cm^{-3}. The systematically absent reflexions were *h*0*l* with *h* odd, and 0*k*0 with *k* odd, and gave the space group as $P2_1/a$, No. 14 in *International Tables for X-ray Crystallography* (1952).

The majority of the intensities were determined photometrically from integrated Weissenberg photographs

Table 2. *Standard deviations of the atom coordinates, in* Å, *and those of the vibration tensor components in* Å^2

	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	$\sigma(U_{11})$	$\sigma(U_{22})$	$\sigma(U_{33})$	$\sigma(2U_{23})$	$\sigma(2U_{13})$	$\sigma(2U_{12})$
K	0·0013 Å	0·0020 Å	0·0014 Å	0·0006	0·0016	0·0008	0·0025	0·0011	0·0024
O(1)	0·0053	0·0061	0·0048	0·0032	0·0047	0·0029	0·0066	0·0050	0·0063
O(2)	0·0054	0·0062	0·0053	0·0031	0·0050	0·0034	0·0072	0·0053	0·0063
C(1)	0·0057	0·0087	0·0065	0·0028	0·0064	0·0036	0·0104	0·0049	0·0102
C(2)	0·0074	0·0091	0·0073	0·0041	0·0068	0·0041	0·0105	0·0066	0·0113
C(3)	0·0084	0·0102	0·0081	0·0052	0·0098	0·0048	0·0104	0·0081	0·0106
C(4)	0·0086	0·0111	0·0079	0·0052	0·0100	0·0046	0·0108	0·0080	0·0115
C(5)	0·0092	0·0108	0·0084	0·0054	0·0093	0·0047	0·0117	0·0082	0·0132
C(6)	0·0097	0·0112	0·0087	0·0058	0·0104	0·0047	0·0119	0·0084	0·0134
C(7)	0·0106	0·0138	0·0087	0·0072	0·0120	0·0053	0·0140	0·0101	0·0157
C(8)	0·0114	0·0160	0·0098	0·0084	0·0147	0·0065	0·0178	0·0120	0·0194
C(9)	0·0167	0·0192	0·0129	0·0158	0·0206	0·0080	0·0202	0·0190	0·0271
C(10)	0·0182	0·0282	0·0154	0·0215	0·0298	0·0100	0·0304	0·0237	0·0398
				$\sigma(U_{\text{iso}})$					
H(1)	0·103	0·106	0·098	0·037					
H(2)	0·163	0·175	0·160	0·076					
H(3)	0·113	0·122	0·106	0·042					
H(4)	0·059	0·071	0·056	0·017					
H(5)	0·087	0·093	0·081	0·028					
H(6)	0·119	0·122	0·121	0·048					
H(7)	0·088	0·087	0·084	0·028					
H(8)	0·085	0·084	0·084	0·027					
H(9)	0·100	0·110	0·098	0·036					
H(10)	0·085	0·095	0·081	0·029					
H(11)	0·083	0·091	0·081	0·029					
H(12)	0·104	0·113	0·101	0·039					
H(13)	0·102	0·102	0·101	0·035					
H(14)	0·127	0·116	0·123	0·047					
H(15)	0·198	0·161	0·210	0·083					
H(16)	0·175	0·138	0·168	0·072					
H(17)	0·133	0·156	0·137	0·060					
H(18)	0·150	0·187	0·140	0·081					
H(19)	0·192	0·195	0·185	0·091					

about both the *a* and *b* axes. Those that were too weak to be measured in this way were determined visually by comparison with a standard set of spots produced by timed exposures of one of the crystal reflexions. The lowest order $00l$ reflexions were recorded on a flat film at a distance of about 11·5 cm. Lorentz, polarization and Tunell factors were corrected for by a computer program written by one of us (ELVL). As the crystal was thin and its linear absorption coefficient was small (35·44 cm^{-1}) for the Cu $K\alpha$ radiation used, no absorption corrections were made at this stage, and no extinction corrections were made. There were 1755 possible reflexions in the region of reciprocal space investigated by us, of which 1036 were observed.

Determination of the structure

The trial structure of VLL was used as the starting point and the *b* axis projection was refined first. The form factors from *International Tables* (1962) were used, and that for each oxygen atom was taken to be the mean of the O and O^- form factors. Hydrogen atoms were neglected at first, and isotropic temperature factors were assumed. Several cycles of least-squares refinement, using the program of D.W.J. Cruickshank, J.G. Sime & J.G.F. Smith (written for the Glasgow KDF9 computer in KALGOL) reduced the residual $R \equiv \Sigma \,||F_o|-|F_c||/\Sigma\, |F_o|$ from 0·40 to 0·20. The most satisfactory weighting scheme for the observations was found to be that of Hughes (1941) in which $\sqrt{w}=1$ for $|F_o| \le p$; and $\sqrt{w}=p/F_o$ for $|F_o|>p$, with $p=12$. The accidentally unobserved reflexions were included in the least-squares refinement by assigning values of $F_o = F_{\min}/\sqrt{3}$ to them, as suggested by Hamilton (1955).

Serious overlapping of the atoms occurs in the *a*-axis projection of this structure so that the *y* coordinates of the atoms could not be accurately determined from two-dimensional refinement. When the three-dimensional data were used in the refinement the *y* coordinates of the atoms received large shifts and some C–C bond lengths assumed unlikely values up to 2·4 Å. The calculated values of structure factors with *h* odd were in very bad agreement with the observed values, although the agreement was reasonably good for those with *h* even. A reconsideration of the trial structure led to the conclusion that all atoms in the asymmetric unit had to be shifted in the *x* direction by a distance $a/4$. When this was done the agreement between observed and calculated structure factors for the *h* odd reflexions was improved and the refinement process then converged until *R* was 0·22. The relation between this new structure and that described by VLL is discussed below. The hydrogen atoms were then included in the structure factor calculations by assuming them to be tetrahedrally disposed about the carbon atoms with C–H bond lengths of 1·08 Å. After further cycles of refinement *R* was reduced to 0·17. Absorption corrections then had to be applied to the observed intensities. Although these corrections were generally small, they were appreciable for reflexions which occurred with nearly grazing incidence, or emergence, from the thin crystal plate. The application of these corrections caused *R* to drop to 0·15.

In the next few cycles, anisotropic temperature factors for the potassium, oxygen and carbon atoms, isotropic temperature factors for the hydrogen atoms and all positional parameters were refined simultaneously.

Calculations of bond lengths, which were made at this stage, showed that some of the C–C bonds differed from the usual value of 1·53 Å for hydrocarbon chains by up to four times the computed standard deviations of the bond lengths. This unpleasant feature of the results disappeared after further cycles of refinement from which the accidentally unobserved reflexions were excluded. The omission of these reflexions caused the calculated bond lengths to come nearer to the normal values and increased slightly the computed values of the standard deviations. The final value of *R*, with unobserved reflexions excluded, was 0·080.

The parameters resulting from the last cycle of refinement are given in Table 1, and the standard devi-

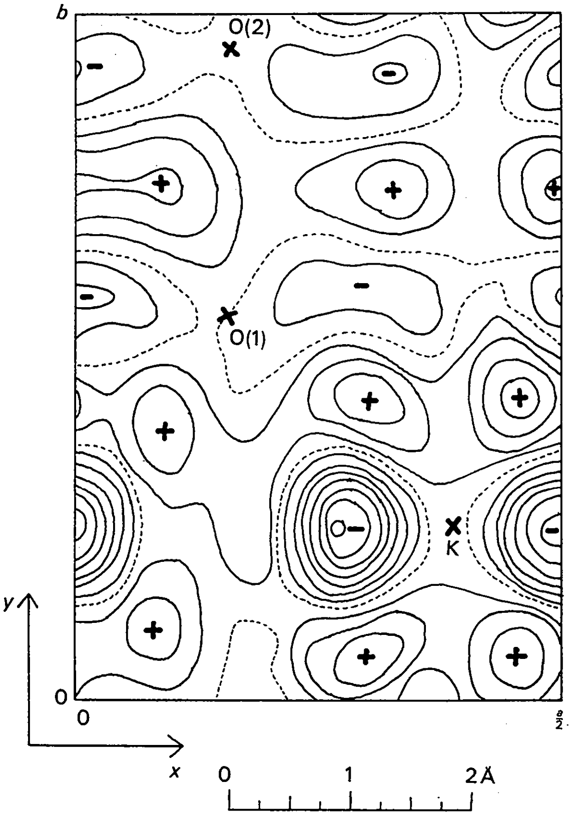

Fig. 1. Map of the difference density in the ionic layer through the potassium ion. Potassium and oxygen centres marked by crosses. Contours at intervals of 0·1 e.Å^{-3}; zero contour dotted. The standard deviation of the difference density is 0·05 e.Å^{-3}.

Table 3. *Observed and calculated structure factors*

The columns give respectively h, k, l, F_o, F_c. Values of F_o and F_c are on an absolute scale.

0	0	27	3.9	3.7
0	0	26	3.9	4.4
0	0	25	11.2	12.9
0	0	24	8.8	9.4
0	0	23	6.5	7.0
0	0	22	9.4	9.7
0	0	21	6.5	6.1
0	0	20	7.0	8.4
0	0	18	6.0	5.0
0	0	17	8.9	-7.8
0	0	16	24.3	-22.3
0	0	14	7.4	-4.1
0	0	13	18.3	18.9
0	0	12	89.1	-85.4
0	0	11	84.2	-84.7
0	0	10	74.1	-71.0
0	0	9	70.7	-71.6
0	0	8	64.1	-64.0
0	0	7	34.9	-37.7
0	0	6	33.8	-37.0
0	0	5	14.4	13.9
0	0	3	67.9	67.3
0	0	2	41.0	36.4
0	0	1	115.0	102.7
2	0	32	3.3	4.6
2	0	31	4.7	5.9
2	0	30	4.2	5.7
2	0	29	4.6	5.8
2	0	28	4.9	6.2
2	0	27	4.6	5.2
2	0	25	3.9	-3.8
2	0	23	7.5	-7.0
2	0	22	11.4	-11.2
2	0	21	15.0	-16.0
2	0	20	17.5	-19.7
2	0	19	23.5	-24.1
2	0	18	23.5	-23.2
2	0	17	26.3	-25.4
2	0	16	22.0	-22.0
2	0	15	16.6	-15.3
2	0	14	20.8	-20.6
2	0	13	29.5	29.1
2	0	12	44.3	42.9
2	0	11	30.7	29.6
2	0	10	40.8	40.0
2	0	9	44.7	43.7
2	0	8	44.5	44.1
2	0	7	41.4	43.9
2	0	6	34.9	34.6
2	0	5	20.1	25.4
2	0	4	12.9	13.0
2	0	3	13.5	-13.2
2	0	1	148.4	-154.9
2	0	0	24.4	-20.5
2	0	-1	120.6	119.8
2	0	-3	26.5	25.8
2	0	-4	4.4	-4.6
2	0	-6	14.4	-14.9
2	0	-7	21.3	-19.6
2	0	-8	25.1	-24.6
2	0	-9	30.5	-30.6
2	0	-10	36.7	-37.5
2	0	-11	20.7	-21.6
2	0	-12	87.8	-82.8
2	0	-13	76.4	-68.0
2	0	-14	8.4	7.7
2	0	-15	7.1	-7.0
2	0	-16	13.0	12.5
2	0	-17	14.2	12.8
2	0	-18	29.4	22.1
2	0	-19	25.2	24.2
2	0	-20	27.0	24.7
2	0	-21	27.5	25.9
2	0	-22	21.4	20.9
2	0	-23	20.0	19.9
2	0	-24	9.0	8.5
2	0	-25	11.3	10.9
2	0	-26	5.6	7.8
2	0	-28	3.8	-4.0
2	0	-29	5.2	-5.3
2	0	-30	6.1	-6.9
2	0	-31	6.7	-7.3
2	0	-32	6.2	-7.2
2	0	-33	4.9	-6.5
2	0	-34	4.4	-5.7
2	0	-35	3.7	-4.2
4	0	26	5.8	-6.9
4	0	24	5.2	-7.6
4	0	23	5.3	-5.3
4	0	22	3.9	-5.7
4	0	21	4.1	-4.3
4	0	16	9.0	7.5
4	0	12	10.9	15.3
4	0	11	22.4	22.1
4	0	10	24.8	26.4
4	0	9	29.5	30.1
4	0	8	29.8	30.7
4	0	7	34.9	32.3
4	0	6	30.6	30.4
4	0	5	24.2	24.6
4	0	4	19.8	19.0
4	0	1	43.1	-37.7
4	0	0	114.9	-110.7
4	0	-1	84.9	-76.5
4	0	-2	66.0	-62.1
4	0	-3	66.0	-61.1
4	0	-4	54.5	-48.0
4	0	-5	19.6	-39.5
4	0	-6	21.8	-21.8
4	0	-8	16.3	15.7
4	0	-9	33.1	30.8
4	0	-10	40.0	36.3
4	0	-11	58.8	53.3
4	0	-12	60.9	59.1
4	0	-13	21.6	21.0
4	0	-14	21.1	21.4
4	0	-15	21.5	23.9
4	0	-16	18.8	15.6
4	0	-17	14.6	13.0
4	0	-18	6.5	5.3
4	0	-21	5.1	-3.2
4	0	-22	8.5	-7.7
4	0	-23	6.5	-5.0
4	0	-24	10.8	-9.6
4	0	-25	14.5	-13.4
4	0	-26	7.1	-6.9
4	0	-27	5.5	-4.9
4	0	-28	5.3	-5.3
4	0	-29	6.1	-5.2
4	0	-30	3.3	-3.9
6	0	21	3.1	3.1
6	0	20	4.8	5.6
6	0	19	7.2	7.1
6	0	18	6.7	8.1
6	0	17	14.1	10.5
6	0	16	14.4	10.9
6	0	15	14.9	13.7
6	0	14	16.7	14.6
6	0	11	4.6	-3.1
6	0	10	7.7	-8.1
6	0	9	13.6	-12.4
6	0	8	16.2	-16.6
6	0	7	17.1	-19.6
6	0	6	16.7	-20.4
6	0	5	17.3	-21.2
6	0	4	14.7	-15.7
6	0	3	14.5	-14.8
6	0	2	9.2	-6.0
6	0	1	17.6	19.5
6	0	0	6.3	7.4
6	0	-1	8.9	-10.2
6	0	-6	3.6	5.1
6	0	-7	6.3	6.6
6	0	-8	8.2	8.7
6	0	-9	10.4	11.7
6	0	-10	11.2	12.6
6	0	-11	11.3	12.1
6	0	-12	27.1	24.6
6	0	-13	27.6	25.0
6	0	-14	12.6	11.6
6	0	-15	9.2	7.8
6	0	-16	4.2	2.7
6	0	-18	6.4	-5.9
6	0	-19	9.7	-9.2
6	0	-20	13.3	-12.3
6	0	-21	13.9	-12.3
6	0	-22	14.4	-13.7
6	0	-23	15.2	-12.2
6	0	-24	7.6	-7.5
6	0	-25	11.4	-10.1
6	0	-26	9.8	-9.7
6	0	-27	4.8	-4.8
8	0	11	5.9	-5.2
8	0	10	6.3	-5.6
8	0	9	7.6	-6.5
8	0	8	7.4	-7.3
8	0	7	9.3	-8.1
8	0	6	8.2	-8.0
8	0	5	9.0	-8.5
8	0	4	8.0	-7.3
8	0	3	5.6	-5.7
8	0	2	7.9	-7.5
8	0	0	15.2	17.2
8	0	-1	15.2	15.1
8	0	-2	13.5	15.9
8	0	-3	14.6	17.9
8	0	-4	13.0	17.7
8	0	-5	11.7	17.0
8	0	-6	11.1	14.6
8	0	-7	10.4	10.3
8	0	-8	5.5	5.6
8	0	-11	11.0	-11.9
8	0	-12	14.1	-15.8
8	0	-13	11.2	-10.5
8	0	-14	9.7	-9.5
8	0	-15	14.0	-11.4
8	0	-16	10.8	-10.3
8	0	-17	9.3	-9.3
8	0	-18	5.6	-8.0
8	0	-19	6.2	-5.8
8	0	-20	4.4	-4.4
8	0	-24	4.0	3.6
8	0	-25	5.6	5.9
8	0	-26	3.7	4.8
8	0	-27	3.0	4.0
0	1	33	3.2	-4.4
0	1	32	5.2	-5.5
0	1	31	4.3	-5.2
0	1	30	3.2	-5.0
0	1	27	3.9	-4.6
0	1	26	4.1	-4.6
0	1	25	3.1	3.4
0	1	24	11.0	11.2
0	1	23	9.5	9.7
0	1	22	4.1	2.5
0	1	21	20.7	19.7
0	1	20	20.7	19.8
0	1	19	23.4	21.8
0	1	18	21.6	22.7
0	1	17	26.6	29.5
0	1	16	39.1	40.7
0	1	15	7.6	7.7
0	1	14	11.7	-9.7
0	1	13	12.8	-12.7
0	1	12	19.1	-18.9
0	1	11	35.2	-36.0
0	1	10	36.9	-39.7
0	1	9	39.8	-42.5
0	1	8	44.6	-47.9
0	1	7	50.2	-50.7
0	1	6	50.0	-51.7
0	1	5	45.0	-46.2
0	1	4	55.9	-55.0
0	1	3	53.6	58.4
0	1	2	17.6	17.0
0	1	1	17.0	-17.4
1	1	23	4.4	-4.5
1	1	22	7.3	7.1
1	1	21	2.2	2.5
1	1	20	3.0	-3.0
1	1	19	2.1	-1.9
1	1	18	6.8	-6.2
1	1	17	7.9	-8.1
1	1	16	12.2	10.7
1	1	15	11.0	11.6
1	1	14	11.7	-13.9
1	1	12	5.8	-4.8
1	1	11	2.0	2.1
1	1	10	6.8	6.7
1	1	9	4.1	3.7
1	1	8	4.5	4.0
1	1	7	1.8	0.8
1	1	6	2.6	1.9
1	1	5	4.9	-5.7
1	1	4	32.3	-36.5
1	1	3	9.0	7.0
1	1	2	66.5	67.2
1	1	1	27.1	-28.6
1	1	0	9.9	10.1
1	1	-1	36.8	-41.5
1	1	-2	25.2	-26.9
1	1	-3	57.8	63.3
1	1	-4	5.2	6.1
1	1	-5	9.6	-10.0
1	1	-6	11.1	-11.0
1	1	-7	3.2	-3.7
1	1	-8	7.2	-6.9
1	1	-10	4.3	-4.0
1	1	-11	14.6	14.0
1	1	-13	9.2	8.5
1	1	-14	10.2	-8.5
1	1	-15	19.1	-19.1
1	1	-16	15.2	16.2
1	1	-17	11.0	9.8
1	1	-19	2.8	-2.7
1	1	-20	2.9	-2.3
1	1	-21	8.9	-9.7
1	1	-22	3.7	3.6
1	1	-23	5.2	6.1
1	1	-24	3.1	-4.2
2	1	30	1.6	1.5
2	1	29	3.0	3.3
2	1	28	3.7	4.5
2	1	27	4.0	5.4
2	1	26	6.9	7.4
2	1	25	6.4	7.2
2	1	24	9.5	9.0
2	1	23	15.7	16.0
2	1	22	8.1	8.4
2	1	21	2.2	2.7
2	1	20	3.2	4.6
2	1	19	2.1	-1.0
2	1	18	3.2	-3.7
2	1	17	18.1	-16.1
2	1	16	7.4	-8.3
2	1	15	2.3	-1.0
2	1	14	10.2	-15.2
2	1	13	26.6	-23.4
2	1	12	29.4	-24.5
2	1	11	33.9	-31.3
2	1	10	38.0	-38.8
2	1	9	34.2	-34.3
2	1	8	31.8	-32.6
2	1	7	23.0	-22.6
2	1	6	20.0	-20.1
2	1	4	22.9	-24.1
2	1	3	1.5	2.2
2	1	2	80.5	78.2
2	1	1	79.2	77.5
2	1	0	82.7	82.1
2	1	-1	87.1	90.5
2	1	-2	119.9	124.2
2	1	-3	37.7	37.9
2	1	-4	14.0	12.6
2	1	-5	28.8	28.0
2	1	-6	4.2	3.9
2	1	-7	2.7	-2.4
2	1	-8	21.8	-23.1
2	1	-9	30.7	-30.7
2	1	-10	45.7	-44.2
2	1	-11	41.2	-40.9
2	1	-12	40.4	-41.0
2	1	-13	40.3	-40.1
2	1	-14	30.1	-31.1
2	1	-15	2.3	0.5
2	1	-16	14.6	-18.7
2	1	-17	27.7	-24.3
2	1	-18	11.5	-10.9
2	1	-19	10.4	-9.7
2	1	-20	3.1	2.4
2	1	-21	4.4	-5.0
2	1	-22	9.0	9.4
2	1	-23	17.4	19.0
2	1	-24	10.9	11.2
2	1	-25	8.9	10.0
2	1	-26	9.5	9.7
2	1	-27	6.9	8.0
2	1	-28	7.0	8.1
2	1	-29	7.6	7.0
2	1	-30	9.2	4.6
2	1	-31	1.8	2.8
2	1	-34	1.9	-2.7
2	1	-35	1.9	-3.7
3	1	17	7.5	-6.2
3	1	16	9.5	-7.7
3	1	15	7.2	7.2
3	1	14	2.5	3.6
3	1	13	2.3	-1.2
3	1	11	3.5	-4.1
3	1	7	3.1	3.0
3	1	6	1.5	1.6
3	1	5	14.8	11.9
3	1	3	20.9	-30.8
3	1	2	8.7	9.0
3	1	1	14.2	13.5
3	1	0	5.0	4.6
3	1	-1	14.3	13.4
3	1	-2	34.4	-33.4
3	1	-3	14.6	-12.6
3	1	-4	18.0	18.9
3	1	-5	9.2	7.7
3	1	-6	1.3	1.0
3	1	-7	1.3	-1.6
3	1	-8	3.4	-4.0
3	1	-10	5.6	-5.6
3	1	-14	13.1	13.2
3	1	-15	10.4	-10.4
3	1	-16	14.1	-11.4
3	1	-17	4.3	4.6
3	1	-18	7.6	7.3
3	1	-20	4.5	5.2
3	1	-22	10.3	-8.4
3	1	-23	4.1	4.1
3	1	-24	2.3	2.4
4	1	21	6.0	-5.3
4	1	20	8.5	-8.3
4	1	19	14.0	-10.3
4	1	18	11.8	-11.4
4	1	17	18.0	-15.9
4	1	16	23.2	-22.9
4	1	15	16.5	-16.1
4	1	14	9.5	-7.9
4	1	13	5.1	-5.2
4	1	11	7.5	8.1
4	1	10	11.5	12.2
4	1	9	20.9	19.0
4	1	8	25.6	24.9
4	1	7	31.0	30.5
4	1	6	31.7	30.5
4	1	5	39.3	37.5
4	1	4	35.5	35.8
4	1	1	9.7	8.1
4	1	0	2.2	2.7
4	1	-1	10.7	-10.0
4	1	-2	8.2	8.4
4	1	-3	17.6	17.7
4	1	-4	14.9	-13.8
4	1	-5	21.7	-19.5
4	1	-6	24.9	-24.0
4	1	-7	28.1	-25.8
4	1	-8	29.5	-26.9
4	1	-9	29.9	-27.1
4	1	-10	29.6	-27.8
4	1	-11	29.4	-27.6
4	1	-12	25.1	-23.2
4	1	-13	19.7	-18.6
4	1	-14	21.1	-21.0
4	1	-15	6.9	-5.8
4	1	-16	10.2	18.7
4	1	-17	16.0	14.6
4	1	-18	15.1	16.9
4	1	-19	17.4	15.8
4	1	-20	20.0	18.9
4	1	-21	20.7	18.5
4	1	-22	8.6	5.5
4	1	-23	11.2	11.3
4	1	-24	13.4	13.6
4	1	-25	8.0	8.5
4	1	-26	4.4	5.1
4	1	-29	1.8	-2.0
4	1	-30	1.8	-3.4
4	1	-31	4.1	-3.8
4	1	-32	3.0	-5.1
4	1	-33	3.3	-4.2
5	1	17	3.8	3.8
5	1	16	4.1	-3.4
5	1	4	11.2	11.0
5	1	3	1.9	-1.7
5	1	2	10.0	-10.4
5	1	-1	11.9	10.1
5	1	-2	7.9	7.4
5	1	-3	14.5	-11.5
5	1	-4	8.8	-8.0

Table 3 (*cont.*)

5	1	-13	4.0	-3.7
5	1	-14	4.1	3.2
5	1	-15	6.5	7.0
5	1	-16	9.5	-4.4
5	1	-17	7.1	-7.0
5	1	-22	5.4	-2.3
5	1	-23	3.6	-3.6
5	1	-24	4.1	1.8
6	1	24	4.2	-4.3
6	1	23	5.8	-6.5
6	1	22	5.1	-5.8
6	1	21	2.8	-3.9
6	1	20	4.5	-3.4
6	1	17	5.2	3.7
6	1	14	4.1	4.2
6	1	13	7.9	7.5
6	1	12	8.5	8.3
6	1	11	10.9	10.7
6	1	10	14.2	12.1
6	1	9	11.1	11.4
6	1	8	11.3	11.5
6	1	7	10.8	12.0
6	1	6	10.2	10.5
6	1	5	7.4	8.2
6	1	4	13.4	11.7
6	1	3	6.6	7.1
6	1	2	9.2	-9.4
6	1	1	22.4	-17.6
6	1	0	22.3	-19.6
6	1	-1	32.6	-29.8
6	1	-2	40.3	-36.9
6	1	-3	31.2	-26.4
6	1	-4	23.8	-20.5
6	1	-5	23.8	-20.2
6	1	-6	18.1	-16.0
6	1	-7	10.4	-9.9
6	1	-8	2.1	-2.4
6	1	-9	4.1	4.8
6	1	-10	11.4	11.9
6	1	-11	15.0	15.4
6	1	-12	16.6	17.2
6	1	-13	20.7	20.7
6	1	-14	19.2	17.5
6	1	-15	7.6	8.0
6	1	-16	11.8	10.9
6	1	-17	15.4	14.5
6	1	-18	12.6	12.3
6	1	-19	9.7	8.9
6	1	-20	2.8	4.6
6	1	-21	8.1	6.6
6	1	-23	7.4	-7.0
6	1	-24	5.4	-6.4
6	1	-25	5.8	-6.0
6	1	-26	6.0	-6.5
6	1	-27	6.2	-6.6
6	1	-28	5.9	-7.3
6	1	-29	5.4	-6.5
6	1	-30	4.1	-5.4
6	1	-31	2.9	-3.8
6	1	-32	1.5	-2.5
7	1	5	3.0	-3.5
7	1	3	4.7	5.4
8	1	16	6.8	6.5
8	1	15	6.6	6.6
8	1	14	5.3	5.5
8	1	13	5.5	5.3
8	1	12	4.4	4.1
8	1	10	2.3	0.3
8	1	8	5.2	-5.6
8	1	7	7.5	-8.2
8	1	6	9.0	-10.2
8	1	5	11.2	-12.5
8	1	4	11.4	-12.5
8	1	3	6.1	-7.9
8	1	2	3.7	-5.2
8	1	1	5.6	-6.4
8	1	0	2.1	-4.0
8	1	-2	2.1	-3.0
8	1	-3	2.1	-3.3
8	1	-5	3.0	4.2
8	1	-6	3.7	5.9
8	1	-7	6.1	6.9
8	1	-8	7.4	8.4
8	1	-9	9.6	9.6
8	1	-10	10.7	10.9
8	1	-11	11.8	12.1
8	1	-12	11.4	10.7
8	1	-13	10.5	10.0
8	1	-14	12.4	10.8
8	1	-15	6.6	6.1
8	1	-16	3.2	-0.6
8	1	-17	3.9	-3.5
8	1	-18	4.6	-4.7
8	1	-19	5.2	-5.5
8	1	-20	8.6	-8.4
8	1	-21	9.9	-9.3
8	1	-22	4.7	-5.3
8	1	-23	5.3	-5.9
8	1	-24	6.1	-6.9
8	1	-25	4.7	-5.8
8	1	-26	3.2	-4.3
0	2	33	4.4	4.8
0	2	32	1.6	2.7
0	2	31	1.5	-3.3
0	2	30	5.3	-4.7
0	2	29	4.3	-5.9
0	2	28	7.9	-8.4
0	2	27	10.6	-10.6
0	2	26	13.0	-12.4
0	2	25	14.0	-13.5
0	2	24	16.0	-15.1
0	2	23	14.6	-13.4
0	2	22	11.0	-10.4
0	2	21	13.7	-13.3
0	2	20	12.3	12.4
0	2	19	32.7	32.8
0	2	18	16.6	16.6
0	2	17	14.5	15.8
0	2	16	21.1	22.9
0	2	15	25.3	25.9
0	2	14	26.3	27.2
0	2	13	25.7	27.4
0	2	12	24.5	23.7
0	2	11	17.3	18.0
0	2	10	10.7	9.2
0	2	8	26.5	-27.4
0	2	7	15.5	-14.9
0	2	6	16.5	16.4
0	2	5	8.7	-9.3
0	2	4	22.6	-21.4
0	2	3	22.2	-25.3
0	2	2	25.5	-29.9
0	2	1	27.5	-33.5
0	2	0	30.1	-34.6
1	2	21	5.1	4.4
1	2	20	2.5	-2.6
1	2	19	7.4	-8.5
1	2	18	6.9	8.3
1	2	11	3.3	1.8
1	2	10	2.3	-1.5
1	2	9	4.8	-4.6
1	2	8	7.8	6.3
1	2	7	7.1	7.6
1	2	6	16.1	-15.6
1	2	0	2.1	2.7
1	2	-1	1.5	-2.0
1	2	-2	3.5	3.8
1	2	-3	6.8	-6.6
1	2	-4	7.1	7.6
1	2	-5	13.4	-13.1
1	2	-6	8.1	9.5
1	2	-7	20.0	19.5
1	2	-8	10.3	-10.2
1	2	-9	3.2	-2.4
1	2	-15	2.3	-1.2
1	2	-16	5.1	-4.7
1	2	-17	5.7	6.4
1	2	-18	7.5	-8.1
1	2	-19	8.7	-7.5
1	2	-20	10.7	10.3
1	2	-22	2.5	-1.5
1	2	-23	3.6	1.1
2	2	22	4.4	5.3
2	2	20	7.8	-7.6
2	2	19	13.8	10.8
2	2	18	25.8	24.5
2	2	17	19.3	20.8
2	2	16	19.2	19.0
2	2	15	21.2	19.3
2	2	14	16.7	17.8
2	2	13	16.8	14.5
2	2	12	12.1	11.1
2	2	11	4.9	4.6
2	2	10	3.9	-5.3
2	2	9	14.3	-13.7
2	2	8	27.1	-27.7
2	2	7	58.3	-60.2
2	2	6	61.7	-65.2
2	2	5	44.4	-46.9
2	2	4	47.3	-49.3
2	2	3	46.8	-48.0
2	2	2	39.3	-39.6
2	2	1	27.2	-27.1
2	2	0	16.6	-16.6
2	2	-2	15.3	15.1
2	2	-3	26.4	30.2
2	2	-4	36.1	38.5
2	2	-5	35.9	35.7
2	2	-6	65.0	70.2
2	2	-7	80.8	87.7
2	2	-8	51.7	54.5
2	2	-9	35.2	36.7
2	2	-10	26.3	28.2
2	2	-11	16.7	15.5
2	2	-12	6.5	6.2
2	2	-13	4.8	-5.1
2	2	-14	12.8	-12.6
2	2	-15	18.7	-19.7
2	2	-16	22.4	-23.5
2	2	-17	24.8	-26.3
2	2	-18	40.8	-40.0
2	2	-19	29.0	-27.4
2	2	-20	5.2	4.9
2	2	-21	2.6	-2.5
2	2	-22	7.4	-7.9
2	2	-23	2.6	-3.5
2	2	-24	2.6	-3.6
2	2	-25	2.5	-2.0
2	2	-31	1.9	0.5
2	2	-33	3.4	4.8
2	2	-34	4.8	5.1
3	2	7	6.4	7.8
3	2	6	4.9	-5.7
3	2	5	3.5	-5.0
3	2	4	5.7	6.2
3	2	3	1.7	0.6
3	2	2	2.8	2.7
3	2	0	1.6	1.9
3	2	-1	2.2	-3.3
3	2	-3	4.9	-5.6
3	2	-4	1.6	1.3
3	2	-5	9.0	8.8
3	2	-6	11.0	-12.4
3	2	-9	1.7	-2.0
3	2	-18	8.9	9.7
3	2	-19	9.2	-9.5
3	2	-21	4.0	4.1
4	2	28	1.3	2.3
4	2	27	2.7	3.9
4	2	26	4.9	5.3
4	2	25	7.4	7.0
4	2	24	9.3	9.2
4	2	23	9.4	9.3
4	2	22	10.2	10.3
4	2	21	14.2	12.5
4	2	20	3.7	2.8
4	2	19	9.0	-8.2
4	2	18	6.3	-6.4
4	2	17	5.2	-5.0
4	2	16	10.6	-8.9
4	2	15	14.8	-12.9
4	2	14	18.1	-18.0
4	2	13	19.8	-18.3
4	2	12	20.3	-18.9
4	2	11	19.5	-17.3
4	2	10	16.1	-14.5
4	2	9	13.1	-10.8
4	2	7	4.9	4.4
4	2	6	5.6	-5.1
4	2	5	2.9	-4.6
4	2	4	8.5	8.8
4	2	3	14.9	13.9
4	2	2	20.5	17.0
4	2	1	22.9	21.6
4	2	0	26.5	23.9
4	2	-1	26.0	24.2
4	2	-2	25.7	22.9
4	2	-3	24.4	21.2
4	2	-4	22.8	21.5
4	2	-5	5.0	3.2
4	2	-6	5.3	-4.8
4	2	-7	10.9	10.5
4	2	-8	11.1	11.9
4	2	-9	3.5	3.7
4	2	-11	7.4	-7.6
4	2	-12	10.1	-10.7
4	2	-13	13.8	-13.0
4	2	-14	15.6	-15.4
4	2	-15	18.2	-16.0
4	2	-16	17.6	-16.0
4	2	-17	11.2	-10.7
4	2	-18	14.2	-15.2
4	2	-19	29.8	-32.5
4	2	-20	21.1	-20.4
4	2	-23	4.9	4.9
4	2	-24	7.6	8.3
4	2	-25	9.9	10.1
4	2	-26	10.7	11.0
4	2	-27	10.9	10.9
4	2	-28	10.6	10.4
4	2	-29	9.0	9.0
4	2	-30	8.1	8.6
4	2	-31	6.7	7.6
5	2	-4	6.8	-6.2
5	2	-6	4.9	3.6
5	2	-8	2.2	-1.3
5	2	-17	5.9	-5.5
5	2	-18	4.4	3.6
5	2	-19	5.7	5.5
6	2	20	2.0	2.2
6	2	19	2.2	-2.0
6	2	18	8.4	-7.1
6	2	17	7.5	-7.7
6	2	16	8.2	-7.7
6	2	15	10.0	-8.0
6	2	14	9.0	-7.9
6	2	13	9.5	-7.8
6	2	12	7.9	-7.1
6	2	11	5.4	-5.3
6	2	8	3.8	5.1
6	2	7	18.9	14.9
6	2	6	22.5	20.1
6	2	5	17.2	17.3
6	2	4	16.9	17.0
6	2	3	18.7	18.8
6	2	2	15.6	17.7
6	2	1	13.9	15.0
6	2	0	9.7	13.1
6	2	-1	6.4	9.4
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6	2	-15	2.7	1.7
6	2	-16	6.3	5.7
6	2	-17	12.6	12.0
6	2	-18	27.2	22.9
6	2	-19	19.9	18.3
6	2	-20	5.7	6.1
6	2	-21	6.3	6.4
6	2	-22	7.3	8.1
6	2	-23	6.0	6.0
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6	2	-25	2.3	3.2
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8	2	12	5.6	6.0
8	2	11	6.1	6.2
8	2	10	6.7	6.3
8	2	9	5.9	5.9
8	2	8	3.7	4.0
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8	2	6	5.9	4.8
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8	2	-7	4.2	-4.1
8	2	-8	4.2	-3.9
8	2	-11	4.2	3.1
8	2	-12	5.0	4.1
8	2	-13	4.5	4.9
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8	2	-17	5.6	3.7
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0	3	14	15.4	-15.8
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2	3	23	12.6	-12.5
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2	3	-5	4.2	-0.3
2	3	-6	15.5	-15.6
2	3	-7	11.0	[illegible]
2	3	-8	9.3	[illegible]
2	3	-10	2.1	[illegible]
2	3	-11	[illegible]	[illegible]

Table 3 (*cont.*)

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3	3	4	9.9	-9.5
3	3	3	3.4	-4.4
3	3	1	4.2	4.0
3	3	-3	11.9	-11.0
3	3	-4	3.7	2.1
3	3	-5	10.8	11.0
3	3	-16	8.8	-9.3
3	3	-17	4.9	-4.6
3	3	-18	6.7	6.7
3	3	-19	3.2	2.2
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3	3	-22	2.8	-1.5
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4	3	18	4.0	4.8
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4	3	16	14.6	13.6
4	3	15	11.6	10.2
4	3	14	13.6	11.0
4	3	13	11.9	10.5
4	3	12	8.9	8.4
4	3	11	5.5	4.9
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4	3	8	14.4	-12.5
4	3	7	16.9	-17.9
4	3	6	29.4	-27.0
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4	3	4	30.8	-27.9
4	3	3	24.3	-21.4
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4	3	-6	37.8	35.0
4	3	-7	38.4	35.3
4	3	-8	30.9	35.1
4	3	-9	35.0	29.7
4	3	-10	25.9	25.1
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4	3	-17	25.1	-25.9
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4	3	-23	3.9	-4.3
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5	3	0	2.5	1.5
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5	3	-5	4.3	-1.7
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6	3	11	11.1	-9.4
6	3	10	9.9	-9.2
6	3	9	7.8	-7.7
6	3	8	6.1	-5.9
6	3	7	2.9	-3.6
6	3	3	3.9	3.4
6	3	2	7.7	8.4
6	3	1	11.8	10.7
6	3	0	15.9	13.0
6	3	-1	15.8	14.4
6	3	-2	20.3	17.0
6	3	-3	17.5	14.6
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6	3	-5	4.6	4.4
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6	3	-14	7.2	-7.8
6	3	-15	5.3	-5.8
6	3	-16	3.1	-4.0
6	3	-17	14.2	-11.3
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6	3	-20	10.8	-11.8
6	3	-21	8.9	-9.1
6	3	-22	2.6	-2.7
6	3	-23	2.3	1.0
6	3	-24	4.3	3.9
6	3	-25	5.6	4.8
6	3	-26	7.4	6.1
6	3	-27	7.7	6.9
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8	3	9	2.1	1.8
8	3	7	2.4	3.8
8	3	6	5.3	6.8
8	3	5	8.2	9.7
8	3	4	10.6	9.2
8	3	3	8.3	7.9
8	3	2	9.6	8.0
8	3	1	8.7	7.6
8	3	0	6.4	6.6
8	3	-1	5.9	5.0
8	3	-2	4.1	4.0
8	3	-3	5.4	4.5
8	3	-4	3.4	1.7
8	3	-5	3.4	-3.8
8	3	-6	7.2	-7.2
8	3	-7	9.9	-9.1
8	3	-8	11.3	-11.1
8	3	-9	12.3	-11.6
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8	3	-11	11.7	-11.7
8	3	-12	11.5	-10.6
8	3	-13	9.5	-8.7
8	3	-14	6.8	-6.4
8	3	-15	3.7	-3.6
8	3	-16	2.7	2.6
8	3	-17	7.4	7.1
8	3	-18	7.2	7.1
8	3	-19	8.8	8.2
8	3	-20	8.4	8.4
8	3	-21	6.4	5.9

ations in Table 2. The values of the observed and calculated structure factors are given in Table 3. A difference electron density map was calculated and showed no significant features except for hollows and peaks in the region of the ionic layer which are shown in Fig. 1. The interpretation of these features is not yet clear to us.

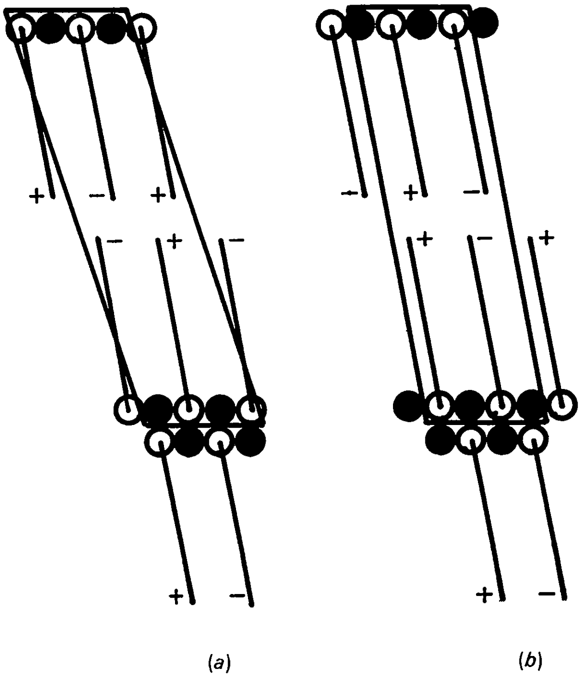

Fig. 2. Relation between the structure proposed by VLL (*a*) and the present structure (*b*). Chains with plus signs are tilted up from the paper; those with minus signs are tilted down.

Discussion of results

The unit-cell dimensions given above agree well with those reported by VLL except for the value of β. Because VLL observed sharp spots only for reflexions having h even, there were two distinct possible independent values for β, and VLL chose that possibility which is wrong for the present structure. The relation between the VLL proposed structure and the present one is illustrated schematically in Fig. 2.

The packing in the ionic layers is the same in both structures and is illustrated in VLL. The present results show that the distances from a potassium atom to its four neighbours in the same half of the double ionic layer are 2·671, 2·688, 2·707 and 2·734 ± 0·006 Å and those to the two neighbours in the other half of the double layer are 2·849 and 2·888 ± 0·008 Å. The carbon–oxygen bond lengths are 1·270 ± 0·010 and 1·250 ± 0·010 Å; they are thus not significantly different and the mean value, 1·260 Å, is a reasonable value for a carbon–oxygen bond of 50% double bond character (Hahn, 1957; Vaughan & Donohue, 1952). The bond lengths between carbon atoms were calculated and are shown in Fig. 3; the average is 1·529 ± 0·008 Å and the average distance between alternate carbon atoms is 2·558 ± 0·009 Å. The average C–C–C bond angle is 113·8 ± 0·5°. These values agree closely with values found in other hydrocarbon chain compounds. The average C–H bond length is 1·09 ± 0·02 Å. The carbon and oxygen atoms in a molecule are very nearly coplanar; the only significant departures of carbon atoms from their mean plane are those of C(2) and C(3) which lie at distances of 0·043 ± 0·007 and 0·031 ± 0·008 Å from it. In contrast to the structure of form *B* of potassium palmitate there is no rotation of the COO group about the C(1)–C(2) bond. It is surprising that there is so little distortion of the potassium caprate molecule from its idealized structure; in the crossed-chain compounds tetradecamide (Turner & Lingafelter, 1955) and 11-aminoundecanoic acid hydrobromide hemihydrate (Sim, 1955) the terminal groups are displaced from the molecule plane.

The packing of the methyl groups is illustrated in Fig. 4. The distances between the carbon atoms of a methyl group and those of the adjacent layer are 4·00, 4·46, 4·46, and 5·54 ± 0·04 Å, and the distances to its neighbours in the same layer are 4·22 ± 0·04 and 5·69 ± 0·02 Å.

Table 4. *Magnitudes and directions of the principal axes of the thermal vibration tensors*

U_i are the magnitudes, in Å^2; g_{ij} are the direction cosines referred to the crystal axes.

	U_i (Å^2)	g_{i1}	g_{i2}	g_{i3}
K	0·0663	0·1683	−0·0367	0·9397
	0·0448	−0·9658	0·1939	0·3405
	0·0378	0·1973	0·9803	−0·0321
O(1)	0·0821	0·6628	0·0191	0·6193
	0·0603	−0·7484	−0·0137	0·7852
	0·0338	0·0229	−0·9997	0·0011
O(2)	0·0876	0·1071	0·1330	0·9508
	0·0676	−0·9703	0·2300	0·2450
	0·0387	−0·2167	−0·9640	0·1897
C(1)	0·0703	−0·0910	−0·2259	0·9707
	0·0423	0·9759	−0·2141	−0·1318
	0·0322	0·1983	0·9503	0·2010
C(2)	0·0809	0·6846	−0·2158	0·5640
	0·0648	−0·6986	0·0784	0·8237
	0·0291	0·2081	0·9733	0·0587
C(3)	0·0896	−0·3797	0·9238	0·1154
	0·0720	0·2413	0·0478	0·9112
	0·0671	−0·8931	−0·3799	0·3954
C(4)	0·1046	0·1068	0·9880	0·0911
	0·0733	0·9566	−0·1328	0·0856
	0·0648	−0·2708	−0·0792	0·9922
C(5)	0·1029	0·5180	0·6859	0·4113
	0·0805	0·6945	−0·6861	0·0904
	0·0614	−0·4994	−0·2426	0·9070
C(6)	0·1144	−0·0401	0·9453	0·3258
	0·0895	0·9860	−0·0143	−0·0109
	0·0635	−0·1619	−0·3260	0·9454
C(7)	0·1710	−0·1139	0·9112	0·4098
	0·1010	0·9642	0·0054	0·0901
	0·0486	−0·2393	−0·4120	0·9077
C(8)	0·2265	−0·0673	0·9328	0·3605
	0·1079	0·9725	−0·0180	0·0564
	0·0603	−0·2230	−0·3600	0·9311
C(9)	0·2660	−0·0106	0·9575	0·2855
	0·1893	0·9690	−0·0613	0·0641
	0·0733	−0·2470	−0·2818	0·9562
C(10)	0·3942	−0·0598	0·9712	0·2376
	0·2400	0·9763	0·0087	0·0401
	0·0857	−0·2082	−0·2381	0·9705

The components U_{ij} of the vibration tensor, reported in Table 1, are defined by $\overline{u_l^2} = \sum_i \sum_j U_{ij} l_i l_j$ where $\overline{u_l^2}$ is the mean square displacement of the atom in the direction defined by the unit vector **l** which has components l_1, l_2 and l_3 referred to the reciprocal unit cell axes. The principal values and axes of the vibration tensor were calculated for each atom from the U_{ij} values in Table 1 with the results shown in Table 4. An examination of these results showed that the directions of maximum and minimum displacement both lay very nearly in the

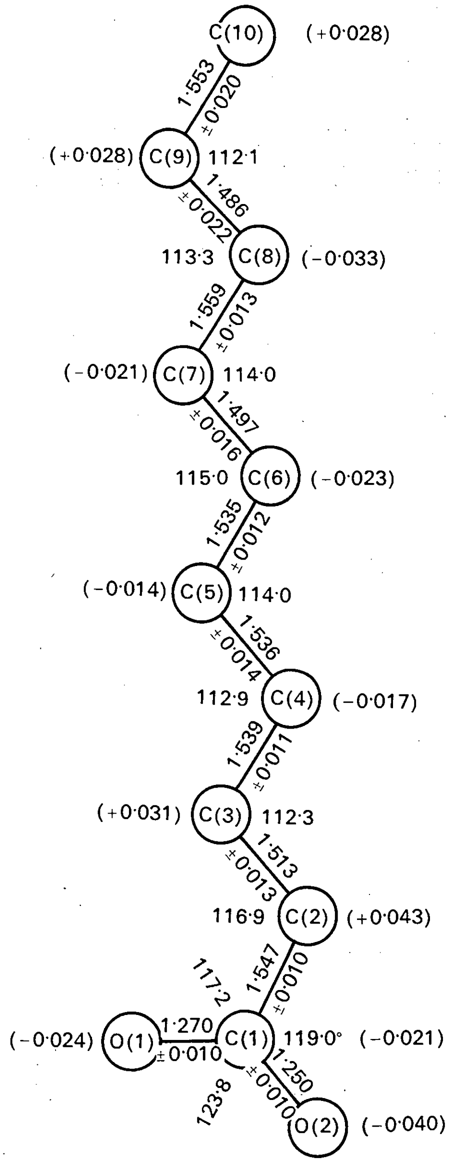

Fig. 3. Dimensions of the caprate ion. All distances are in Å. Figures in parentheses are the deviations (Å) of the atoms from the mean plane of the carbon atoms. The calculated standard deviations of the angles are about 1·2° at the bottom of the chain, increasing to about 3·0° at the top end.

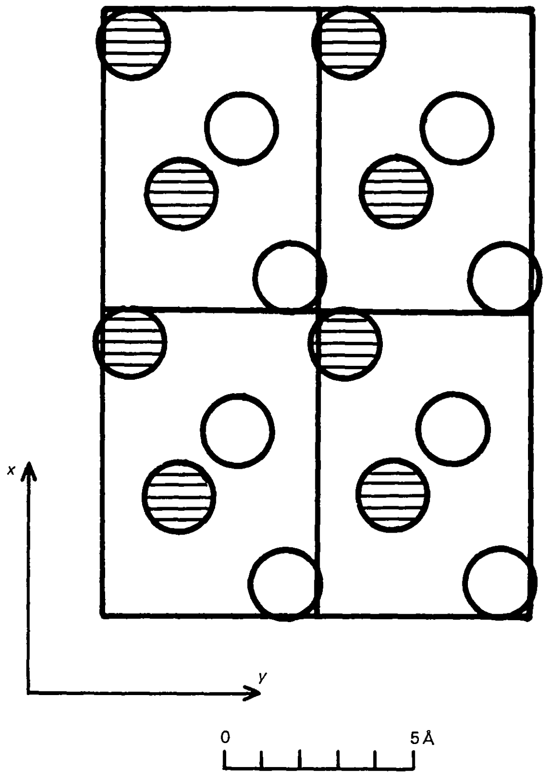

Fig. 4. Arrangement of the methyl groups in the crystal. Shaded circles represent methyl groups in one layer; open circles those in the other layer.

plane of the hydrocarbon chain for many of the carbon atoms, and that the direction of maximum displacement, for those atoms showing marked anisotropic motions, was perpendicular to the hydrocarbon chain axis. The directions and magnitudes of the thermal vibrations can be visualized from Fig. 5. In a preliminary investigation of the high temperature *C* form of potassium caprate Dumbleton (1964) has shown that the structure is similar to that of the *A* form except for the position of the last four carbon atoms in the hydrocarbon chain. It is interesting to note the marked increase in the root mean square displacements of these last four carbon atoms in the *A* form structure and to speculate on the relevance of these large thermal motions to the mechanism of the phase change between the *A* and *C* forms.

The effect of including the unobserved reflexions in the least-squares refinement is interesting. A similar effect has been observed in the refinement of hexatriacontane by Dunning & Vand (1967) and it appears that at the present time the safest way to deal with these reflexions is to omit them completely from the refinement.

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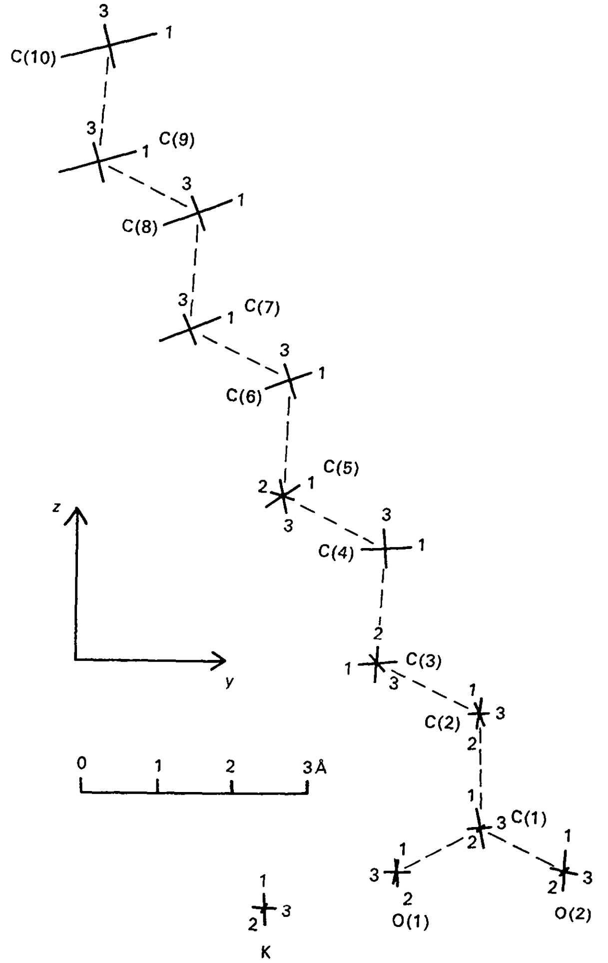

Fig. 5. Principal axes of the r.m.s. thermal vibration amplitudes of the potassium, oxygen and carbon atoms, projected onto the mean plane of the carbon atoms. The numbers 1, 2 and 3 refer to the maximum, medium and minimum axes respectively; these numbers appear on that end of the principal axis pointing upwards from the paper. The medium vibration (No. 2) for the atoms C(4) and C(6) to C(10) is perpendicular to the paper. The vibration amplitudes and the molecule dimensions are drawn to the same scale.

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Structure Cristalline des Composés Intermétalliques T_4Co_3 (T=Y, Gd, Tb, Dy, Ho, Er et Tm)

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The crystal structure of intermetallic compounds T_4Co_3, where T is yttrium or a rare earth metal of the second series, has been determined on a single crystal with composition $Ho_4Co_{3,07}$. The crystallographic unit cell is hexagonal; its parameters are $a=11,4$, $c=3,99$ Å. The space group is $P6_3/m$. One of the three Co sites is only partially filled at random.

Introduction

Les diagrammes d'état établis entre le cobalt et un métal de terre rare ou l'yttrium présentent, suivant les auteurs, des composés intermétalliques différents dans la zone de composition comprise entre la phase de Laves TCo_2 et la phase la plus riche en terre rare T_3Co. Novy, Vickery & Kleber (1961) signalent l'existence des composés Gd_2Co_3 et GdCo; Strnat, Ostertag, Adams & Olson (1965) celle de Y_2Co_3 et Y_3Co_2; Pelleg & Carlson (1965) en plus des deux précédents suggèrent YCo. Wood & Conard (1964) ne proposent qu'un composé de formule Dy_3Co_2 avec le dysprosium et Buschow (1966) que le composé Er_2Co avec l'erbium. Nous avons préparé des composés de formule T_4Co_3 avec les éléments terre rare de la deuxième série et l'yttrium. Nous présentons ici leur structure et précisons le domaine de composition de cette nouvelle phase.

Preparation et données experimentales

La pureté des éléments de départ était 99,9% pour les métaux de terre rare et 99,99% pour le cobalt. La méthode de préparation utilisée était la fusion sans creuset par lévitation haute fréquence suivie d'une trempe brutale sur une lingotière de cuivre. Nous avons réussi à préparer un monocristal avec l'holmium de la façon suivante: les constituants ont été fondus par induction à 1350°C sous atmosphère d'hélium dans un creuset d'alumine; la composition du bain correspondait à 3 atomes d'holmium pour 2 atomes de cobalt. Après refroidissement nous avons observé dans l'alliage des cavités où s'étaient formés de petits cristaux ayant la forme d'aiguilles. Le cristal choisi pour l'étude de la structure avait une forme de prisme hexagonal d'épaisseur 0,1 mm et de longueur 2 mm environ. Nous ne connaissions pas sa composition exacte. L'indexation d'un cliché de cristal tournant autour de l'axe de l'aiguille nous a montré que la maille du cristal était hexagonale avec l'axe **c** parallèle à l'axe de l'aiguille. Les paramètres de cette maille étaient $a=11,40\pm0,05$ Å et $c=3,99\pm0,01$ Å.

Nous avons enregistré les taches de diffraction *hk*0, *hk*1, *hk*2 et *hk*3 à l'aide d'une chambre de Weissenberg intégrante par la méthode d'équi-inclinaison. Nous avons ainsi observé 288 réflexions indépendantes. Nous

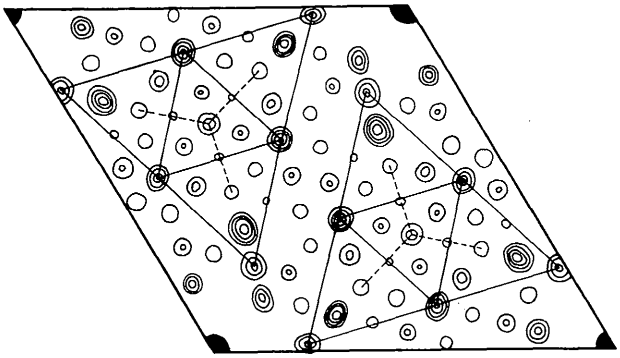
Fig. 1. Projection de Patterson parallèle à l'axe **c**.