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The Crystal Structure of $KCeS_2$

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The crystal structure of $KCeS_2$ has been determined by single-crystal X-ray diffraction techniques. The compound crystallizes with the rhombohedral α-$NaFeO_2$ structure, $a=4{\cdot}228$, $c=21{\cdot}80$ Å (hexagonal setting). Full-matrix least-squares refinement, assuming $R\bar{3}m$ symmetry, of 307 observed symmetry-independent three-dimensional diffractometer data (Mo $K\alpha$) gave a conventional R index of 0·023 ($R_{wF}=0{\cdot}024$). Both cations are coordinated octahedrally; the possibility of a trigonal prismatic coordination of one of the cations was rejected on the basis of the refinement results. Refinement under $R3m$ symmetry yielded no significant improvement of R_{wF}. Under the assumption that $R\bar{3}m$ is the right space group, the structure can be regarded as a layer-ordered NaCl structure, in which the close-packed sulphur layers are displaced towards the cerium layers.

Introduction

Since 1964, compounds of the type $MLnS_2$ (M = Li, Na, K; Ln = rare earth ion) have been known. Ballestracci & Bertaut (1964) and Ballestracci (1965) determined their structures by X-ray powder measurements. They reported these compounds to crystallize with the α-$NaFeO_2$ structure, space group $R\bar{3}m$, or the NaCl structure.

For several reasons, however, it seems important to perform a single-crystal X-ray study of these sulphides. The ascertainment of the space group from powder data is ambiguous. It is important to establish definitely whether the coordination of the cations is octahedral or trigonal prismatic (Jellinek, 1960). For the interpretation of the physical properties of these compounds, *e.g.* crystal field splitting, spectra and magnetic properties at low temperatures, the exact value of the positional parameter of the sulphur ions is of interest. Finally, the crystal chemistry of the $MLnS_2$ compounds has not been studied in detail. Bronger, Elter, Maus & Schmitt (1973) found the rubidium and some of the caesium compounds to have the α-$NaFeO_2$ structure too; so the same structure would occur for a wide range of the radius ratio of the cations ($0{\cdot}62 < r^{3+}_{Ln}/r^{+}_{M} < 1{\cdot}23$).

Experimental

Crystals of $KCeS_2$ were prepared by heating a mixture of CeO_2 (99·9%, Alfa Inorganics) and an excess of K_2S (p.a. Merck) in a stream of H_2S. After cooling from 1000°C (30°/h) the product was washed with water and acetone, and dried. Unit-cell dimensions, derived from powder diffractograms, are $a=4{\cdot}228$ (4), $c=21{\cdot}80$ (1) Å (hexagonal axes). The calculated density for $Z=3$ and a molecular weight of 243·4, $d=3{\cdot}59$ g cm^{-3}, agrees with the measured density, $d=3{\cdot}61$ g cm^{-3}. A hexagonal-shaped crystal of approximate size $0{\cdot}1\times0{\cdot}1\times0{\cdot}05$ mm was mounted on an Enraf–Nonius three-circle single-crystal diffractometer, with the hexagonal a axis along the φ axis.

Intensities were recorded by the θ–2θ scan method for all reflexions with θ between 5 and 40°, using graphite monochromatized Mo $K\alpha$ radiation. Background intensities were determined at $\theta\pm\frac{1}{2}\Delta$, where $\Delta=0{\cdot}8+1{\cdot}2\tan\theta$. The mean counting time was 36 s for each background and 72 s for the scan. The total number of reflexions measured by this method was 1740. Reflexions with intensities less than twice the standard deviation, calculated from counting statistics, were considered as not significant. All data were corrected for Lorentz and polarization effects and for absorption (de Graaff, 1973), using transmission factors between 0·13 and 0·41 ($\mu=118{\cdot}0$ cm^{-1}).

All intensities were reduced to F values and an averaging procedure was carried out, giving a total number of 307 observed symmetry-independent reflexions. Starting values for the scaling factor and the initial overall isotropic thermal parameter B were obtained from a calculated Wilson plot.

Refinement of the structure

The function minimized during the least-squares refinement process was $\sum w_F(|F_o|-|F_c|)^2$, with the weighting factor $w_F=(\sigma_F)^{-2}$. Discrepancy indices referred to are: $R_F=\sum||F_o|-|F_c||/\sum|F_o|$ and $R_{wF}=[\sum w_F(|F_o|-|F_c|)^2/\sum w_F|F_o|^2]^{1/2}$.

From zero-and upper-level Weissenberg photographs the crystal symmetry and the approximate cell parameters were determined. Systematically absent reflexions were of the type $-h+k+l\neq3n$, indicating a rhombohedral symmetry, and the intensities of the reflexions $hkil$ and $kh\bar{i}\bar{l}$ were equal. The Laue group appeared to be $\bar{3}m$, leaving three possible space groups: $R\bar{3}m$, $R3m$ and $R32$.

Two models with both cations in an octahedral coordination and two models with either Ce or K in a

Table 1. *Positions for the atoms in the different space groups*

Positions			Space group	Cation coordination
Ce	3(*a*)	0,0,0	$R\bar{3}m$ and $R32$	both octahedral
K	3(*b*)	$0,0,\frac{1}{2}$		
S	6(*c*)	$0,0,z$ $0,0,\bar{z}$ $\}\ z\simeq\frac{1}{4}$		
Ce	3(*a*)	$0,0,z;\ z=0$	$R3m$	both octahedral
K	3(*a*)	$0,0,z;\ z\simeq\frac{1}{2}$		
S(1)	3(*a*)	$0,0,z;\ z\simeq\frac{1}{4}$		
S(2)	3(*a*)	$0,0,z;\ z\simeq\frac{3}{4}$		
Ce	3(*a*)	$0,0,z;\ z=0$	$R3m$	Ce octahedral
K	3(*a*)	$0,0,z;\ z\simeq\frac{5}{6}$		K prismatic
S(1)	3(*a*)	$0,0,z;\ z\simeq\frac{5}{12}$		
S(2)	3(*a*)	$0,0,z;\ z\simeq\frac{7}{12}$		
Ce	3(*a*)	$0,0,z;\ z\simeq\frac{5}{6}$	$R3m$	Ce prismatic
K	3(*a*)	$0,0,z;\ z=0$		K octahedral
S(1)	3(*a*)	$0,0,z;\ z\simeq\frac{5}{12}$		
S(2)	3(*a*)	$0,0,z;\ z\simeq\frac{7}{12}$		

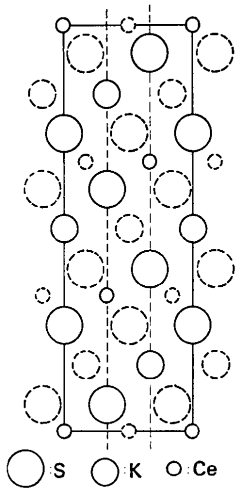

Fig. 1. Projection on $(11\bar{2}0)$ of $KCeS_2$.

trigonal prismatic coordination, were refined by a full-matrix least-squares method. The positions for the atoms in the different space groups, according to these models, are given in Table 1. Refinement of both prismatic models (with either Ce or K on $z\simeq\frac{5}{6}$) gave poor results: the best R_F value obtained was 0·40.

For the octahedral model, however, refinement under $R\bar{3}m$ or $R3m$ symmetry of only the scaling factor and the overall thermal parameter yielded $R_F=0{\cdot}17$. Three cycles of full-matrix refinement under $R\bar{3}m$ symmetry of the positional parameter of sulphur and the isotropic thermal parameters of all atoms reduced R_F to 0·04. At this stage the thermal parameters were allowed to refine anisotropically and an extinction correction was carried out. This led to final discrepancy indices, considering $R\bar{3}m$ symmetry, $R_F=0{\cdot}023$ and $R_{wF}=0{\cdot}024$. Having reached this level, it can be stated already that $R\bar{3}m$ is the most likely space group. The low indices R_F and R_{wF}, the low value of the parameter U_{33} of sulphur and the absence of chemical arguments for lowering the symmetry strongly indicate this. Still it was thought useful to attempt a refinement under $R3m$ symmetry, decoupling the sulphur positions and allowing the z parameter of K to refine also, with the expectation that adding new parameters to be refined would reduce the discrepancy indices to a lower level. We carried out three refinements under $R3m$ symmetry. First the K position was kept exactly at $(0,0,\frac{1}{2})$ and the displacements of S(1) and S(2) were restricted to be equal and in the same direction for both sulphur ions ($\Delta z_{S(1)}=\Delta z_{S(2)}$). Then, in the second refinement the z parameter of K was allowed to refine also. Finally, the z parameters of K(1), S(1) and S(2) were all refined independently. In all cases the anisotropic thermal parameters of all atoms were refined as well, the starting values being the final values from the refinement under $R\bar{3}m$. The thermal parameters for the sulphur atoms 1 and 2 were restricted to keep equal values for both atoms. The results are summarized in Table 2.

Table 2. *Positional and thermal parameters* ($\times 10^4$) *for* $KCeS_2$

The general anisotropic temperature factor has the form $\exp[-2\pi^2(\sum\sum U_{ij}h_ih_ja_i^*a_j^*)]$. Owing to the site symmetry of the ions there are several restrictions on the thermal parameters U_{ij}: $U_{11}=U_{22}=2U_{12}$; $U_{23}=U_{31}=0$. Estimated standard deviations in the least significant digits are in parentheses.

Space group		x	y	z	$U_{11}=U_{22}=2U_{12}$	U_{33}	R_F(%)	R_{wF}(%)
$R\bar{3}m$	Ce	0	0	0	69 (1)	94 (1)	2·29	2·36
	K	0	0	5000	181 (3)	134 (4)		
	S	0	0	2634·6 (4)	105 (2)	103 (3)		
$R3m$(1)	Ce	0	0	0	69 (1)	95 (1)	2·30	2·29
	K	0	0	5000	180 (3)	130 (4)		
	S(1)	0	0	2652 (3)	99 (2)	78 (7)		
	S(2)	0	0	7382 (3)	99 (2)	78 (7)		
$R3m$(2)	Ce	0	0	0	69 (1)	95 (1)	2·30	2·28
	K	0	0	5010 (10)	181 (3)	121 (12)		
	S(1)	0	0	2647 (6)	99 (2)	84 (8)		
	S(2)	0	0	7377 (6)	99 (2)	84 (8)		
$R3m$(3)	Ce	0	0	0	69 (1)	95 (1)	2·30	2·28
	K	0	0	5018 (15)	181 (3)	110 (25)		
	S(1)	0	0	2643 (7)	99 (2)	88 (8)		
	S(2)	0	0	7374 (7)	99 (2)	88 (8)		

As can be seen, refinement under $R3m$ gives a slight improvement of the index R_{wF}. However, this improvement is not very significant because of the almost complete correlation of the sulphur parameters, U_{33} and z, which are refined, as is shown by the correlation matrices. So we conclude that $R\bar{3}m$ is the most likely space group for $KCeS_2$. The observed and calculated structure factors in that space group are listed in Table 3.

Table 3. *Structure factors*

H	K	L	FOBS	FCALC
0	0	3	4520	4017
0	0	6	4243	3845
0	0	9	1601	1464
0	0	12	5941	5432
0	0	15	3857	3657
0	0	18	3538	3380
0	0	21	801	746
0	0	24	2262	2185
0	0	27	2038	2027
0	0	33	850	846
0	0	36	941	944
0	0	39	694	728
1	0	-38	1672	1696
1	0	-35	1018	1035
1	0	-32	1150	1168
1	0	-29	778	784
1	0	-26	2855	2801
1	0	-23	2633	2530
1	0	-20	3005	2888
1	0	-17	851	831
1	0	-14	3568	3389
1	0	-11	3936	3823
1	0	-8	6718	6459
1	0	-5	2145	2082
1	0	-2	3405	3555
1	0	1	2738	2909
1	0	4	7811	7722
1	0	7	4145	3908
1	0	10	3719	3523
1	0	13	1125	1064
1	0	16	4281	3877
1	0	19	3251	3061
1	0	22	3184	3053
1	0	25	727	734
1	0	28	1548	1551
1	0	31	1480	1460
1	0	34	2087	2091
1	0	37	825	851
2	-1	0	5974	6766
2	-1	3	3077	3171
2	-1	6	3185	3141
2	-1	9	1477	1418
2	-1	12	4674	4546
2	-1	15	3368	3255
2	-1	18	3065	2993
2	-1	21	704	712
2	-1	24	2016	1930
2	-1	27	1872	1876
2	-1	30	2373	2338
2	-1	33	805	808
2	-1	36	870	889
2	0	-37	821	812
2	0	-34	1935	1933
2	0	-31	1344	1366
2	0	-28	1419	1434
2	0	-25	692	703
2	0	-22	2812	2766
2	0	-19	2852	2788
2	0	-16	3499	3414
2	0	-13	1043	1013
2	0	-10	3006	2957
2	0	-7	3297	3310
2	0	-4	5627	5977
2	0	-1	2412	2496
2	0	2	2846	2944
2	0	5	1916	1903
2	0	8	5112	5247
2	0	11	3387	3339
2	0	14	3006	2940
2	0	17	802	792
2	0	20	2718	2597
2	0	23	2416	2326
2	0	26	2627	2561
2	0	29	748	750
2	0	32	1086	1091
2	0	35	935	980
3	-1	-35	907	930
3	-1	-32	999	1023
3	-1	-29	705	721
3	-1	-26	2366	2351
3	-1	-23	2153	2145
3	-1	-20	2375	2359
3	-1	-17	754	752
3	-1	-14	2613	2610
3	-1	-11	3038	2997
3	-1	-8	4612	4517
3	-1	-5	1740	1735
3	-1	-2	2423	2490
3	-1	1	2156	2229
3	-1	4	4820	5037
3	-1	7	2852	2935
3	-1	10	2601	2573
3	-1	13	957	954
3	-1	16	3133	3050
3	-1	19	2619	2554
3	-1	22	2593	2522
3	-1	25	663	675
3	-1	28	1301	1331
3	-1	31	1251	1281
3	-1	34	1765	1792
3	0	-33	704	743
3	0	-30	1980	1991
3	0	-27	1574	1621
3	0	-24	1645	1681
3	0	-21	647	654
3	0	-18	2474	2442
3	0	-15	2725	2692
3	0	-12	3539	3535
3	0	-9	1284	1226
3	0	-6	2296	2310
3	0	-3	2423	2482
3	0	0	4497	4763
3	0	3	2455	2482
3	0	6	2281	2310
3	0	9	1231	1226
3	0	12	3528	3535
3	0	15	2737	2692
3	0	18	2480	2442
3	0	21	653	654
3	0	24	1592	1681
3	0	27	1614	1621
3	0	30	1989	1991
3	0	33	716	743
4	-2	0	4045	4227
4	-2	3	2266	2250
4	-2	6	2078	2056
4	-2	9	1155	1142
4	-2	12	3288	3188
4	-2	15	2517	2477
4	-2	18	2255	2232
4	-2	21	622	632
4	-2	24	1541	1536
4	-2	27	1438	1514
4	-2	30	1832	1844
4	-2	33	680	714
4	-1	-31	1113	1136
4	-1	-28	1125	1153
4	-1	-25	617	533
4	-1	-22	2114	2126
4	-1	-19	2149	2168
4	-1	-16	2553	2524
4	-1	-13	858	849
4	-1	-10	2063	2054
4	-1	-7	2429	2437
4	-1	-4	3847	3842
4	-1	-1	1799	1951
4	-1	2	1993	1935
4	-1	5	1445	1458
4	-1	8	3546	3597
4	-1	11	2518	2495
4	-1	14	2151	2139
4	-1	17	568	588
4	-1	20	1581	1381
4	-1	23	1838	1842
4	-1	26	2713	1333
4	-1	29	698	671
4	-1	32	892	907
4	0	-29	628	649
4	0	-26	1843	1851
4	0	-23	1717	1714
4	0	-20	1832	1828
4	0	-17	705	663
4	0	-14	1953	1958
4	0	-11	2300	2295
4	0	-8	3257	3253
4	0	-5	1347	1362
4	0	-2	1713	1748
4	0	1	1606	1706
4	0	4	3487	3559
4	0	7	2203	2224
4	0	10	1850	1880
4	0	13	793	806
4	0	16	2333	2312
4	0	19	1399	2037
4	0	22	1945	1952
4	0	25	575	515
4	0	28	1077	1087
4	0	31	1084	1074
5	-2	-29	605	629
5	-2	-26	1704	1718
5	-2	-23	1587	1599
5	-2	-20	1686	1692
5	-2	-17	681	641
5	-2	-14	1811	1802
5	-2	-11	2154	2118
5	-2	-8	3012	2966
5	-2	-5	1304	1271
5	-2	-2	1594	1597
5	-2	1	1557	1581
5	-2	4	3180	3238
5	-2	7	2065	2052
5	-2	10	1727	1726
5	-2	13	772	770
5	-2	16	2134	2127
5	-2	19	1863	1864
5	-2	22	1815	1816
5	-2	25	590	599
5	-2	28	1032	1022
5	-1	-27	1227	1251
5	-1	-24	1239	1258
5	-1	-21	587	583
5	-1	-18	1737	1749
5	-1	-15	1342	1343
5	-1	-12	2405	2431
5	-1	-9	938	951
5	-1	-6	1554	1558
5	-1	-3	1734	1768
5	-1	0	3033	3137
5	-1	3	1726	1768
5	-1	6	1529	1558
5	-1	9	937	951
5	-1	12	2393	2431
5	-1	15	1944	1949
5	-1	18	1752	1749
5	-1	21	597	583
5	-1	24	1262	1258
5	-1	27	1258	1251
5	0	-25	547	571
5	0	-22	1586	1568
5	0	-19	1643	1619
5	0	-16	1826	1818
5	0	-13	714	712
5	0	-10	1480	1478
5	0	-7	1766	1764
5	0	-4	2696	2712
5	0	-1	1356	1375
5	0	2	1341	1363
5	0	5	1131	1120
5	0	8	2460	2498
5	0	11	1802	1822
5	0	14	1538	1547
5	0	17	592	607
5	0	20	1452	1463
5	0	23	1339	1403
6	-3	0	2538	2637
6	-3	3	1530	1532
6	-3	6	1376	1341
6	-3	9	876	861
6	-3	12	2118	2067
6	-3	15	1713	1689
6	-3	18	1531	1510
6	-3	21	554	559
6	-3	24	1120	1106
6	-2	-22	1451	1462
6	-2	-19	1496	1515
6	-2	-16	1702	1687
6	-2	-13	697	688
6	-2	-10	1385	1375
6	-2	-7	1665	1644
6	-2	-4	2470	2495
6	-2	-1	1267	1289
6	-2	2	1259	1269
6	-2	5	1345	1359
6	-2	8	2303	2300
6	-2	11	1710	1698
6	-2	14	1463	1440
6	-2	17	580	592
6	-2	20	1380	1366
6	-2	23	1329	1318
6	-1	-20	1277	1278
6	-1	-17	584	580
6	-1	-14	1347	1344
6	-1	-11	1589	1586
6	-1	-8	2132	2125
6	-1	-5	993	1003
6	-1	-2	1166	1196
6	-1	1	1199	1213
6	-1	4	2268	2302
6	-1	7	1525	1536
6	-1	10	1275	1295
6	-1	13	656	667
6	-1	16	1571	1571
6	-1	19	1430	1421
6	0	-15	1404	1389
6	0	-12	1680	1654
6	0	-9	787	751
6	0	-6	1127	1101
6	0	-3	1271	1266
6	0	0	2130	2077
6	0	3	1289	1266
6	0	6	1126	[illegible]
6	0	9	755	761
6	0	12	[illegible]	1654
6	0	15	1419	1383
7	-3	-14	1211	1181
7	-3	-11	1435	1394
7	-3	-8	1837	1829
7	-3	-5	937	917
7	-3	-2	1768	1748
7	-3	1	1792	1743
7	-3	4	2017	1973
7	-3	7	1381	1352
7	-3	10	1153	1131
7	-3	13	638	632
7	-2	-12	1559	1542
7	-2	-9	743	733
7	-2	-6	1232	1234
7	-2	-3	1185	1194
7	-2	0	1903	1907
7	-2	3	1177	1194
7	-2	6	1217	1238
7	-2	9	733	722
7	-2	12	1537	1542
7	-1	-4	1832	[illegible]
7	-1	-1	[illegible]	[illegible]
7	-1	2	929	938
7	-1	5	819	833

All calculations were carried out using the Leiden University IBM 360/65 computer, with the aid of a set computer programs, written or modified by Dr R. A. G. de Graaff and Mrs E. W. Rutten-Keulemans.

Discussion

The structure can be described as an ordering in the cation positions in the NaCl structure, or as the $MgCl_2$ structure in which the Mg positions are occupied by the Ce ions and the vacant octahedral positions by the K ions. The projection of the structure on $(11\bar{2}0)$ is given in Fig. 1.

The regular S_6 octahedra of the idealized structure are distorted: the CeS_6 octahedron is compressed (reduced c/a ratio is 0·7205) and the KS_6 octahedron is elongated (reduced c/a 0·9982) along the threefold axis (*cf.* Fig. 2). As could be expected, the octahedra with the highest charged cations are the least distorted ones.

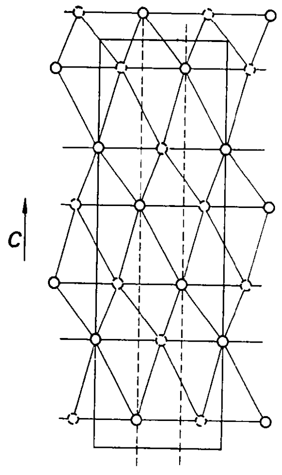

Fig. 2. Projection on $(11\bar{2}0)$, showing the shift of the sulphur layers.

The size of the distortion from the ideal structure can also be described by a position parameter ε, indicating the shift of the sulphur ions (Brunel, de Bergevin & Gondrand, 1972). From the determined z parameter for the sulphur ion in $KCeS_2$ we obtain $\varepsilon_{\text{obs}} = -0{\cdot}0135\ (9)$. Considering the ions as hard spheres one can calculate ε according to the following formula:

$$\varepsilon = \frac{1}{4} - \frac{(r^{3+}_{\text{Ce}} + r^{2-}_{\text{S}})}{2(r^{3+}_{\text{Ce}} + r^{+}_{\text{K}} + 2r^{2-}_{\text{S}})}$$

(in units of the hexagonal c axis). Using the ionic radii given by Shannon & Prewitt (1969) we obtain $\varepsilon_{\text{calc}} = -0{\cdot}0148$, which is in fairly good agreement with the observed value.

A remaining question is what kind of ordering will occur in the case where the alkali ion is much smaller than the rare-earth ion. An attempt to prepare single crystals of some Li compounds is in progress in order to solve this problem.

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