Table VI

Possible $(\mathrm{B_{10}H_8})\underset{\mathrm{H}}{\overset{\mathrm{H}}{<\,>}}(\mathrm{B_{10}H_8})^{2-}$ Isomers

No.[a]	Bridge locations[b]	Pairs linked[c]	Point group[d]
1	1–2′, 2–1′	A–A	$2/m = C_{2h}$
2	1–1′, 2–2′	A–A	$mm2 = C_{2v}$
3	2–3′, 3–2′	E–E	$mm2 = C_{2v}$
4	2–2′, 3–3′	E–E	$2/m = C_{2h}$
5	2–2′, 6–9′	E′–E′	$2/m = C_{2h}$
6a	2–2′, 6–6′	E′–E′	$222 = D_2$
6b	2–2′, 9–9′		
7a	1–2′, 2–3′	A–E	$1 = C_1$
7b	1–3′, 2–2′		
8a	1–2′, 2–6′	A–E′	$1 = C_1$
8b	1–2′, 2–9′		
9a	2–2′, 3–6′	E–E′	$1 = C_1$
9b	2–2′, 3–9′		

[a] The a–b pairs are enantiomers. [b] Reference 11. [c] A denotes an apex–equatorial pair, E denotes a pair in the same equatorial ring, and E′ denotes a pair which has one member in each ring. [d] In Hermann–Mauguin and Schoenflies notations, respectively.

which may be so constructed, five of which are symmetric and the remaining eight of which form four enantiomorphic pairs. Other isomers involving bridging to nonadjacent atoms were not considered because of the drastic crowding of the pair of B–H groups which lie between any such nonadjacent pair. The thirteen isomers are listed in Table VI, together with the point groups to which they belong and an indication of which pairs of atoms in each polyhedron are involved in the hydrogen bridges. The isomer found in this investigation is the fifth listed in Table VI, while no. 1 was proposed[10] for the structure of the parent $B_{20}H_{18}^{2-}$ ion before it was shown[6,7] to be linked by a pair of B–B–B three-center bonds rather than hydrogen bridges. Hawthorne and Pilling mention[3] "the formation of unidentified metastable intermediates" in the thermal reversion of the photoisomer studied here to the parent ion. Thus it may be that some or all of the isomers discussed here also exist.

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Structure of Gadolinium Sesquisulfide

By C. T. PREWITT and A. W. SLEIGHT

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The structure of Gd_2S_3 has been solved and refined by least-squares procedures to an R of 0.019 using 540 nonequivalent reflections collected with a counter diffractometer. Crystals were grown in a GdI_3 melt at 1200°. The crystals are orthorhombic with $a = 7.339$ Å, $b = 15.273$ Å, $c = 3.932$ Å, $D_m = 6.14$ g cm^{-3}, $D_x = 6.187$ g cm^{-3} for $Z = 4$, and space group Pnam. Two kinds of nonequivalent gadolinium atoms are present in Gd_2S_3. One is surrounded by a monocapped trigonal prism of sulfur atoms while the other gadolinium atom is in a bicapped trigonal prism of sulfur atoms. This structure is found for rare earth sesquisulfides from La through Dy and probably also for Pu_2S_3.

Introduction

Very little structural information has been available on rare earth sesquisulfides. (Rare earths will be considered to be La through Lu plus Y and Sc.) The structure of Sc_2S_3, determined by Dismukes and White,[1] is related to the NaCl structure. Apparently, this structure exists for certain rare earth sesquiselenides and sesquitellurides[2,3] but not for any other rare earth sesquisulfide.

According to Flahaut,[4] there are five possible structures for the rare earth sesquisulfides other than that of Sc_2S_3. Two rare earth sulfides, Yb_2S_3 and Lu_2S_3, have the corundum structure.[5] Five—Dy_2S_3, Y_2S_3, Er_2S_3, Ho_2S_3, and Tm_2S_3—have a monoclinic structure. Sesquisulfides from La through Tb can have a defect Th_3P_4-type structure which actually exists over a range of compositions. In addition, Flahaut[4] stated, mainly on the basis of powder patterns, that there are two unknown structures which are referred to as α and β types. A comparison of the powder pattern of Nd_2S_3 reported by Picon, *et al.*,[6] with a powder pattern of our Gd_2S_3 crystals indicated that our crystals are of the general α-sesquisulfide structure type. Since this structure has been found for sesquisulfides of La through Dy[7] and also for Pu_2S_3[8] and since suitable single crystals were prepared for the first time, an investigation of the Gd_2S_3 structure was undertaken.

Experimental Section

Synthesis.—Crystal sponge gadolinium metal (99.9%) was obtained from the Lunex Co. Sulfur was 99.999%, and iodine was reagent grade resublimed. The three reactants were sealed

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[2] J. P. Dismukes and J. G. White, *ibid.*, **4**, 970 (1965).

[3] J. Flahaut, L. Pierre, M. Pardo, and M. Guittard, *Bull. Soc. Chim. France*, 1399 (1965).

[4] J. Flahaut, M. Guittard, M. Patrie, M. P. Pardo, S. M. Golabi, and L. Domange, *Acta Cryst.*, **19**, 14 (1965).

[5] J. Flahaut, L. Domange, and M. Pardo, *Compt. Rend.*, **258**, 594 (1964).

[6] M. Picon, L. Domange, J. Flahaut, M. Guittard, and M. Patrie, *Bull. Soc. Chim. France*, 221 (1960).

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TABLE I

OBSERVED AND CALCULATED STRUCTURE FACTORS[a]

h	10F_o	10F_c
K,L= 0, 0		
2	2361	2314
4	302	300
6	223	211
8	1999	2049
K,L= 1, 0		
1	191	176
2	1992	1971
3	629	627
4	697	684
5	1317	1340
6	766	770
7	1212	1227
8	477	468
9	859	878
K,L= 2, 0		
0	0	8*
1	138	113
2	1284	1202
3	1550	1583
4	2803	2919
5	1691	1728
6	1803	1903
7	234	238
8	156	171
9	192	179
K,L= 3, 0		
1	1098	1055
2	160	159
3	2017	2087
4	135	143
5	193	184
6	989	1010
7	364	367
8	883	902
9	200	207
K,L= 4, 0		
0	2024	1790
1	3169	2878E
2	1626	1645
3	1180	1204
4	339	385
5	301	295
6	283	279
7	691	693
8	487	501
9	1184	1194
K,L= 5, 0		
1	1829	1791
2	793	798
3	1321	1349
4	677	666
5	128	135
6	468	459
7	1703	1726
8	849	834
9	370	355
K,L= 6, 0		
0	601	607
1	588	582
2	142	142
3	2529	2600
4	149	132
5	2445	2522
6	0	26*
7	804	791
8	275	278
9	377	362
K,L= 7, 0		
1	1587	1579
2	1238	1238
3	1756	1782
4	1007	1010
5	752	744
6	226	121
7	1718	1736
8	448	424
K,L= 8, 0		
0	2447	2437
1	2377	2318
2	1474	1492
3	838	840
4	611	625
5	183	176
6	224	219
7	924	907
8	904	912
K,L= 9, 0		
1	446	360
2	1307	1321
3	1525	1531
4	147	127
5	230	221
6	1399	1396
7	118	101
8	1117	1116
K,L=10, 0		
0	341	334
1	801	805
2	1322	1317
3	469	477
4	2151	2139
5	421	417
6	1849	1863
7	341	333
8	118	73
K,L=11, 0		
1	112	100
2	1100	1087
3	323	325
4	524	507
5	561	569
6	417	429
7	904	905
K,L=12, 0		
0	3177	3114
1	491	493
2	1655	1657
3	146	154
4	53	71
5	296	300
6	100	70
7	0	45*
K,L=13, 0		
1	105	106
2	1109	1170
3	253	244
4	497	509
5	720	717
6	571	547
7	807	786
K,L=14, 0		
0	216	48*
1	132	139
2	510	504
3	1223	1230
4	2132	2143
5	1542	1570
6	975	991
K,L=15, 0		
1	1096	1111
2	44	22
3	1146	1158
4	303	292
5	22	70*
6	692	700
K,L=16, 0		
0	581	587
1	2120	2091
2	475	462
3	407	401
4	291	259
5	151	164
K,L=17, 0		
1	707	717
2	330	333
3	715	728
4	182	147
K,L=18, 0		
0	267	177
1	534	519
2	62	57
3	1167	1153
K,L= 0, 1		
2	1640	1653
4	191	165
6	1705	1742
8	1947	1996
K,L= 1, 1		
0	1181	1151
1	2410	2339
2	564	541
3	1813	1828
4	1319	1314
5	949	966
6	1075	1082
7	816	812
8	442	446
9	670	683
K,L= 2, 1		
1	87	40*
2	2673	2748
3	1259	1266
4	1380	1414
5	90	77
6	629	602
7	213	205
8	202	195
9	122	89
K,L= 3, 1		
0	3047	2625E
1	135	118
2	1944	2010
3	1975	1981
4	261	260
5	2262	2342
6	693	691
7	563	569
8	966	990
9	431	422
K,L= 4, 1		
1	1302	1307
2	864	888
3	879	880
4	206	172
5	1067	1078
6	1037	1045
7	1899	1937
8	766	773
9	581	589
K,L= 5, 1		
0	2611	2467
1	2488	2437
2	1743	1752
3	708	708
4	1302	1324
5	1437	1445
6	969	979
7	166	155
8	899	898
K,L= 6, 1		
1	1337	1332
2	484	452
3	1321	1335
4	126	129
5	712	720
6	331	306
7	281	255
8	75	32*
K,L= 7, 1		
0	1339	1349
1	1955	1941
2	1090	1095
3	62	31*
4	2149	2208
5	910	905
6	1128	1136
7	98	84
8	608	611
K,L= 8, 1		
1	168	153
2	549	551
3	541	536
4	148	137
5	936	949
6	878	867
7	1058	1037
8	888	896
K,L= 9, 1		
0	2374	2301
1	186	163
2	1258	1251
3	1692	1712
4	41	17*
5	1966	2027
6	62	1*
7	461	452
8	843	846
K,L=10, 1		
1	204	196
2	2024	2031
3	591	589
4	1064	1079
5	129	123
6	378	381
7	187	163
K,L=11, 1		
0	1706	1710
1	1646	1642
2	220	211
3	1231	1243
4	1259	1275
5	887	910
6	904	914
7	717	706
K,L=12, 1		
1	302	302
2	1284	1307
3	907	925
4	97	89
5	518	501
6	1582	1585
7	489	487
K,L=13, 1		
0	44	48
1	1868	1845
2	217	202
3	770	767
4	1083	1096
5	248	239
6	604	589
K,L=14, 1		
1	658	655
2	922	938
3	1110	1118
4	809	814
5	193	182
6	99	47*
K,L=15, 1		
0	1020	1032
1	0	45*
2	1121	1112
3	937	942
4	455	453
5	1200	1216
K,L=16, 1		
1	751	746
2	456	473
3	368	379
4	104	10*
5	440	435
K,L=17, 1		
0	1165	1157
1	1062	1076
2	1329	1317
3	489	495
4	590	588
K,L=18, 1		
1	703	717
2	325	330
3	1170	1175
K,L= 0, 2		
0	5137	4995E
2	1892	1907
4	267	247
6	203	189
8	1823	1864
K,L= 1, 2		
1	131	142
2	1652	1618
3	477	475
4	588	587
5	1159	1164
6	686	682
7	1095	1105
8	429	426
K,L= 2, 2		
0	223	13*
1	104	104
2	1007	999
3	1324	1307
4	2452	2478
5	1514	1504
6	1659	1688
7	227	213
8	149	157
K,L= 3, 2		
1	872	870
2	240	208
3	1724	1722
4	125	120
5	162	161
6	907	895
7	341	331
8	812	823
K,L= 4, 2		
0	1471	1460
1	2422	2396
2	1284	1312
3	978	946
4	343	324
5	292	259
6	252	249
7	635	624
8	460	457
K,L= 5, 2		
1	1412	1420
2	651	655
3	1128	1144
4	588	575
5	164	118
6	433	408
7	1560	1560
8	751	760
K,L= 6, 2		
0	434	445
1	467	473
2	119	111
3	2174	2212
4	128	115
5	2215	2225
6	131	25*
7	721	716
8	252	256
K,L= 7, 2		
1	1290	1299
2	1037	1045
3	1491	1524
4	873	862
5	666	660
6	89	108
7	1557	1575
8	394	388
K,L= 8, 2		
0	2070	2055
1	1985	1970
2	1257	1272
3	724	727
4	551	551
5	186	157
6	198	195
7	618	625
K,L= 9, 2		
1	333	329
2	1130	1141
3	1326	1337
4	129	112
5	202	198
6	1276	1262
7	217	93*
K,L=10, 2		
0	283	291
1	689	696
2	1144	1149
3	416	419
4	1900	1901
5	390	373
6	1678	1690
7	309	305
K,L=11, 2		
1	100	98
2	950	956
3	298	288
4	445	453
5	512	514
6	389	390
K,L=12, 2		
0	2782	2747
1	434	439
2	1471	1470
3	148	139
4	113	64
5	280	271
6	110	69
K,L=13, 2		
1	108	97
2	1032	1046
3	225	219
4	464	460
5	699	652
6	506	501
K,L=14, 2		
0	188	44*
1	138	126
2	446	453
3	1096	1112
4	1936	1947
5	1438	1433
K,L=15, 2		
1	992	1004
2	82	21*
3	1035	1052
4	269	266
K,L=16, 2		
0	529	531
1	1919	1898
2	418	420
3	372	385
4	290	238
K,L=17, 2		
1	639	654
2	335	303
3	646	667
K,L=18, 2		
0	183	160
1	487	474
K,L= 0, 3		
2	1154	1162
4	131	123
6	1378	1397
K,L= 1, 3		
0	817	836
1	1606	1643
2	354	353
3	1302	1321
4	981	1000
5	755	757
6	868	670
7	667	667
K,L= 2, 3		
1	88	84
2	1875	1909
3	930	927
4	1077	1071
5	88	61
6	511	487
7	185	169
K,L= 3, 3		
0	1852	1864
1	19	58*
2	1378	1425
3	1451	1459
4	205	199
5	1826	1843
6	582	560
7	480	469
K,L= 4, 3		
1	889	909
2	616	630
3	659	659
4	110	132
5	862	853
6	867	847
7	1581	1601
K,L= 5, 3		
0	1706	1722
1	1696	1730
2	1242	1285
3	524	529
4	1005	1023
5	1154	1149
6	811	795
7	125	129
K,L= 6, 3		
1	955	975
2	325	334
3	1005	1019
4	117	101
5	594	578
6	274	251
7	235	212
K,L= 7, 3		
0	979	988
1	1400	1439
2	815	829
3	88	23*
4	1694	1739
5	733	726
6	927	931
K,L= 8, 3		
1	145	122
2	418	421
3	415	417
4	146	109
5	765	769
6	722	713
K,L= 9, 3		
0	1746	1759
1	156	127
2	945	970
3	1320	1350
4	27	16*
5	1653	1654
6	0	1*
K,L=10, 3		
1	159	154
2	1557	1599
3	461	472
4	855	873
5	103	103
K,L=11, 3		
0	1320	1352
1	1268	1299
2	210	170
3	986	1001
4	1037	1041
5	753	753
K,L=12, 3		
1	237	243
2	1019	1055
3	734	755
4	109	73
5	433	416
K,L=13, 3		
0	45	42
1	1477	1495
2	172	164
3	612	629
4	899	908
K,L=14, 3		
1	528	536
2	743	770
3	904	924
K,L=15, 3		
0	852	853
1	104	38*
2	907	923
K,L= 0, 4		
0	3293	3254
2	1307	1285
4	178	178
K,L= 1, 4		
1	74	95
2	1143	1094
3	368	351
4	450	417
5	858	855
K,L= 2, 4		
0	57	11*
1	87	68
2	691	677
3	927	908
4	1772	1767
5	1109	1105
K,L= 3, 4		
1	588	583
2	151	145
3	1230	1200
4	100	86
5	127	119
K,L= 4, 4		
0	993	981
1	1606	1621
2	906	900
3	710	701
4	202	235
5	222	193
K,L= 5, 4		
1	968	968
2	459	457
3	818	807
4	429	417
5	128	87
K,L= 6, 4		
0	314	308
1	329	325
2	111	79
3	1573	1582
4	89	82
5	1678	1663
K,L= 7, 4		
1	903	913
2	742	741
3	1087	1103
4	650	649
K,L= 8, 4		
0	1465	1457
1	1410	1400
2	897	914
3	532	530
4	403	411
K,L= 9, 4		
1	239	234
2	817	831
3	978	984
K,L=10, 4		
0	203	212
1	516	510
2	840	846
3	324	311
K,L=11, 4		
1	78	68
2	716	710
K,L=12, 4		
0	2025	2048
1	335	323
K,L= 1, 5		
0	540	547
1	1083	1077
K,L= 2, 5		
1	81	57
K,L= 3, 5		
0	1223	1231
1	100	39*

[a] For each set of fixed k and l, the columns are h, $10F_o$, and $10F_c$. Unobserved reflections and those for which the secondary extinction correction was greater than 25% are marked by an asterisk and E, respectively.

in an evacuated silica ampoule in an atomic ratio of 1:1:1. The ampoule was heated very slowly to avoid a violent reaction which can cause considerable container attack as well as frequent failure. After the reaction was complete, possibly forming GdSI, the temperature was raised to 1200° for about 20 hr.

After the ampoule was cooled to room temperature and opened, red needle-like crystals of Gd_2S_3 were found along with GdI_3. The GdI_3 was washed away with water. Although the odor of H_2S was present, the crystals of Gd_2S_3 were relatively unaffected by the washing. This method of crystal preparation has been found generally applicable for rare earth sesquisulfides.[7] *Anal.* Calcd for Gd_2S_3: Gd, 76.6; S, 23.4. Found: Gd, 76.4; S, 22.2. Iodine was undetectable by X-ray fluorescence.

X-Ray Data.—For Gd_2S_3 the formula weight is 410.68 and a = 7.339 ± 7 Å, b = 15.273 ± 2 Å, and c = 3.9318 ± 4 Å. The least-squares refinement of deWolff-Guinier photograph data was done at 25°. High-purity KCl (a = 6.29310 Å), obtained from Johnson, Matthey & Co., was used as an internal standard. For the crystal we have: $V = 440.70 \pm 5$ Å^3; $D_m = 6.14 \pm 5$ g cm^{-3} (displacement method); $Z = 4$; $D_x = 6.187$ g cm^{-3}; $\mu = 167$ cm^{-1} (Ag Kα). Approximate crystal dimensions are: 0.0034 × 0.0067 × 0.04 cm, with the longest dimension parallel to c. The space group is Pnam-D_{2h}^{16} or Pna2$_1$-C_{2v}^{9} (absences, from precession photographs: $0kl$, $k + l \neq 2n$; $h0l$, $h = 2n$). The space group Pnam was confirmed by the absence of piezoelectric effect, by examination of Patterson maps, and by analysis of refinement results.

Structure Solution and Refinement

Three-dimensional diffraction intensities were measured with a Picker automatic diffractometer using Pd-filtered Ag Kα radiation at a take-off angle of 3° and a scintillation detector. Reflections were scanned for 1.5° plus the α_1-α_2 dispersion, and 40-sec backgrounds were measured at the extremes of each scan. The half-maximum width of the 020 reflection ($2\theta = 4.21°$) was 0.28°, thus indicating that the mosaicity of the crystal is relatively small. In making background corrections, a linear background dependence between each extreme was assumed. Prismatic crystal absorption corrections resulting in transmission factors varying from 0.41 to 0.67 were computed using the method of Wuensch and Prewitt.[9] In all, 567 reflections in one octant of reciprocal space were recorded. Several medium to strong sets of symmetry-equivalent reflections were checked to see that they were equivalent in intensity; however, no statistical studies were made of these sets. The maximum 2θ was 43°.

From three-dimensional Pattersons maps, the locations of two nonequivalent gadolinium atoms were determined, assuming space group Pnam. A subsequent electron density map computed with signs determined by Gd(1) and Gd(2) was sufficient to locate S(1), S(2), and S(3). All atoms lie on mirror planes in equipoint 4c ($x, y, {}^1/_4$; $\bar{x}, \bar{y}, {}^3/_4$; ${}^1/_2 - x, {}^1/_2 + y, {}^3/_4$; ${}^1/_2 + x, {}^1/_2 - y, {}^1/_4$). A few cycles of refinement with a full-matrix, least-squares program SFLS5[10] in which $\Sigma w||F_o| - |F_c||^2$ was minimized, reduced R ($R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$) to 0.06. σ terms for each reflection were computed using

$$\sigma_{F_o} = (LpT)^{-1/2}[(I + \sigma_I)^{1/2} - I^{1/2}]$$

where L, p, and T are the Lorentz, polarization, and transmission factors, respectively, I is the integrated intensity, and

$$\sigma_I = \left[E + \left(\frac{T_E}{2T_B}\right)^2(B_1 + B_2) + \epsilon^2 I^2\right]^{1/2}$$

Here E is the total count plus background, T_E and T_B are peak and background times, B_1 and B_2 are background counts, and ϵ, set in this case to 0.03, accounts for fluctuations in the direct beam and other uncertainties.

Further refinement in which the anisotropic temperature factors and the secondary-extinction parameter C[11,12] [$C = 0.219(8) \times 10^{-5}$] were varied

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Table II

Final Atom Parameters[a]

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}
Gd(1)	14237 ± 5	20418 ± 2	$^1/_4$	00238 ± 9	00065 ± 2	0072 ± 3	−00018 ± 2
Gd(2)	23363 ± 5	45671 ± 2	$^3/_4$	00245 ± 9	00058 ± 2	0072 ± 3	−00001 ± 2
S(1)	0086 ± 2	3914 ± 1	$^1/_4$	0026 ± 3	00078 ± 7	0081 ± 11	−0001 ± 1
S(2)	1253 ± 2	0670 ± 1	$^3/_4$	0023 ± 3	00054 ± 6	0074 ± 10	0001 ± 1
S(3)	3507 ± 2	2814 ± 1	$^3/_4$	0024 ± 3	00053 ± 6	0086 ± 11	0000 ± 1

[a] Points at the left of each decimal entry are omitted.

reduced R to 0.019 and $wtdR$ to 0.027 for 540 reflections included in the refinement. Excluded were 3 strong reflections for which the extinction correction was greater than 25% and 24 unobserved reflections. If the 3 strong reflections are included, R increases to 0.020. The standard deviation of an observation of unit weight was 1.50. Table I gives the final observed and calculated structure factors. Form factors for neutral Gd and S were taken from Cromer and Waber.[13] Real and imaginary anomalous dispersion factors for Ag Kα radiation from Cromer[14] were applied in the usual way.

Atomic coordinates and anisotropic temperature factors are listed in Table II. Interatomic distances and angles plus the magnitudes and orientations of the thermal ellipsoid were calculated[15] and are given in Figures 1 and 2 and Table III.

Table III

Magnitudes and Orientations of Thermal Ellipsoids

		Rms amplitude, Å	B^a	Angles (deg) of r_i with respect to		
				a	b	c
Gd(1)	r_1	0.075 ± 2	0.45	90	90	0
	r_2	0.077 ± 2	0.47	150 ± 3	121 ± 3	90
	r_3	0.091 ± 2	0.65	121 ± 3	31 ± 3	90
Gd(2)	r_1	0.075 ± 2	0.45	90	90	0
	r_2	0.082 ± 1	0.53	165 ± 44	105 ± 44	90
	r_3	0.083 ± 1	0.54	105 ± 44	15 ± 44	90
S(1)	r_1	0.080 ± 5	0.50	90	90	0
	r_2	0.083 ± 5	0.54	169 ± 14	101 ± 14	90
	r_3	0.097 ± 4	0.74	101 ± 14	11 ± 14	90
S(2)	r_1	0.074 ± 5	0.43	138 ± 19	48 ± 19	90
	r_2	0.076 ± 5	0.46	90	90	180
	r_3	0.085 ± 5	0.56	48 ± 19	42 ± 19	90
S(3)	r_1	0.079 ± 5	0.49	100 ± 82	10 ± 82	90
	r_2	0.082 ± 5	0.53	170 ± 82	100 ± 82	90
	r_3	0.082 ± 5	0.53	90	90	0

[a] $B_i = 8\pi^2 r_i^2$.

Discussion

Figures 1 and 3 are diagrams of the Gd_2S_3 structure. Figure 1 shows the bonds and atom positions, and Figure 3 is a stereographic view. The structure is composed of GdS_7 and GdS_8 polyhedra which are linked in a complex way to form a three-dimensional structure. The coordination of Gd(1) is by eight sulfur atoms in a bicapped trigonal prism at average distances of 2.90 Å, and Gd(2) is coordinated by seven sulfur atoms in a distorted monocapped trigonal prism at average distances of 2.82 Å. A capped trigonal prism arrangement seems to be a common coordination for rare earths and actinides. In Sm_2O_3 (B rare earth sesquioxide structure) there are monocapped trigonal prisms.[16] Many rare earth and actinide halides have the $PuBr_3$ structure,[17] which has bicapped trigonal prisms. The rare earth coordination in $LaTe_2$ and

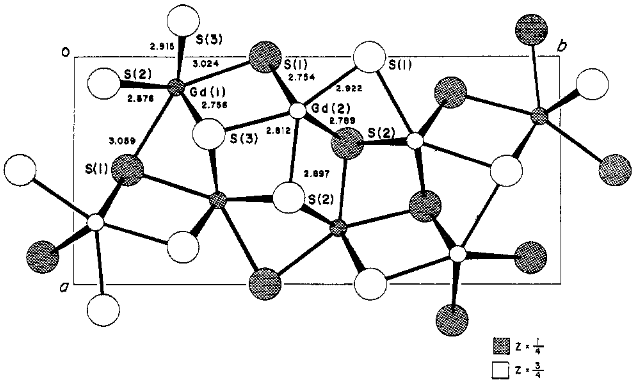

Figure 1.—Model of the Gd_2S_3 structure.

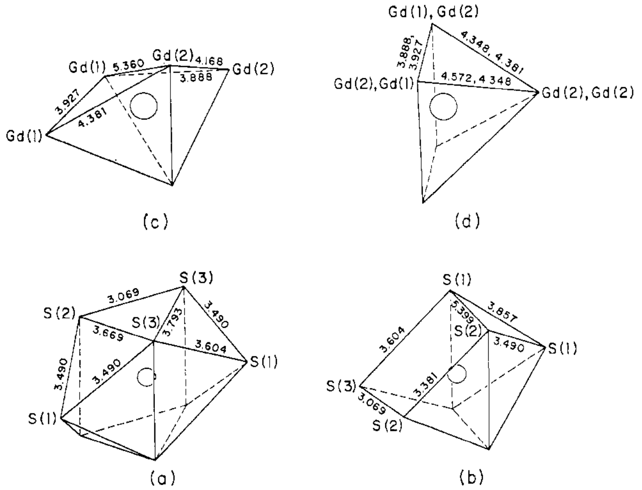

Figure 2.—Coordination polyhedra around (a) Gd(1), (b) Gd(2), (c) S(1), (d) S(2) and S(3). The lengths of the polyhedral edges are the S–S distances in (a) and (b) and the Gd–Gd distances in (c) and (d). In (d), the values corresponding to S(2) are given first. The vertical edges of the polyhedra are all equal to c, *i.e.*, 3.932 Å.

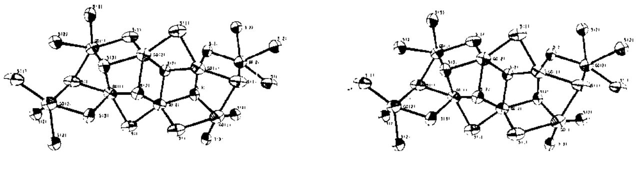

Figure 3.—Stereographic view of the Gd_2S_3 structure.

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$NdTe_2$[18] may be described as a tricapped trigonal prism.

The sulfur atoms in Gd_2S_3 are all coordinated by five gadolinium atoms. A trigonal-bipyramidal arrangement is found for S(1) with average S–Gd distances of 2.90 Å, and S(2) and S(3) are in square pyramids with average S–Gd distances of 2.85 and 2.83 Å, respectively. Figure 2 shows the coordination polyhedra associated with each atom. The S–S distances are all greater than 3.40 Å except for one of 3.04 Å between S(2) and S(3) centered around the point 0.37, 0.48, $^3/_4$ in Figure 1. This short S(2)–S(3) distance represents a polyhedral edge shared between two Gd(1) polyhedra and one Gd(2) polyhedron and is the only edge shared by more than two of the gadolinium polyhedra. There are, however, no unusually short Gd–Gd distances in the structure, the shortest being one of 3.888 Å between Gd(1) and Gd(2). This is consistent with the magnetic data[7] which indicate very weak interactions between gadolinium atoms. For Gd_2S_3 there are no magnetic transitions down to 4.2°K, the Curie–Weiss constant (θ) is -8°K, and the observed moment of 7.94 ± 0.01 BM is in excellent agreement with the calculated value[19] of 7.94 BM.

Recently, a structure for monoclinic Ho_2S_3 has been reported[20] which contains half of the Ho in octahedral and half in sevenfold coordination. Thus the coordination of the rare earth is showing a general tendency to increase as the size of the rare earth increases, going from six in the corundum type, through mixed six and seven in the monoclinic type, to mixed seven and eight in the orthorhombic type.

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Magnetic, Mössbauer, and Structural Studies on Three Modifications of $FeMoO_4$

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Three modifications of $FeMoO_4$ have been characterized by magnetic susceptibility, Mössbauer effect, and X-ray studies. The low-temperature, low-pressure form, α-$FeMoO_4$, is isostructural with low-temperature $NiMoO_4$ and $CoMoO_4$. The high-temperature, low-pressure form, β-$FeMoO_4$, is isostructural with $MnMoO_4$ and $MgMoO_4$ and exists metastably at room temperature when quenched from above 600°. The high-pressure form, $FeMoO_4$-II, represents a triclinic distortion of the monoclinic $NiWO_4$-type structure. Magnetic and Mössbauer results indicate high-spin divalent iron to be present in all three modifications. Antiferromagnetic interactions in $FeMoO_4$-II lead to magnetic order below 45°K.

Introduction

At least two forms of $FeMoO_4$ are known to exist. A low-pressure modification, α-$FeMoO_4$, was first prepared by Schultze[1] as monoclinic prisms from a fused-salt reaction. This product has also been reported by others,[2–6] and the X-ray diffraction powder pattern has been presented.[2,6,7] Its structure has generally been believed to be different from those of the normal (STP) forms of all other $A^{2+}Mo^{6+}O_4$-type molybdates (where A may be Mg, Mn, Co, Ni, Zn, and Cu).[8–10] Abrahams[11] states that normal (STP) $FeMoO_4$ is probably triclinic. Young and Schwartz[12] have reported a high-pressure modification, $FeMoO_4$-II, which they found to be structurally related to $NiWO_4$.

The purpose of this investigation was to identify the various modifications of $FeMoO_4$ and to compare their properties. It was of particular interest to determine if the reportedly unique structure for α-$FeMoO_4$ might be due to an unusual valence combination, *i.e.*, Fe^{3+}-$Mo^{5+}O_4$, instead of $Fe^{2+}Mo^{6+}O_4$.

Experimental Section

All forms of $FeMoO_4$ could be prepared from an appropriate mixture of Fe_2O_3, MoO_3, and Mo or Fe_2O_3, MoO_3, and Fe. The reactants, obtained from Johnson, Matthey & Co., were all at least 99.99% pure. Both low-pressure forms of $FeMoO_4$ were prepared by heating the intimately mixed reactants in evacuated platinum or silica tubes at 900–1000° for 1–2 days. Depending on the cooling rate, the product was α-$FeMoO_4$, β-$FeMoO_4$, or a mixture of these two forms. α-$FeMoO_4$ was also prepared by mixing stoichiometrically solutions of $FeCl_2$ and Na_2MoO_4 at about 100° and then drying the precipitate at 400° under vacuum.

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