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CRYSTAL STRUCTURE OF KH_2F_3 AND GEOMETRY OF THE $H_2F_3^-$ ION*

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Crystals of KH_2F_3 contained in polyethylene tubes, because of the high vapor pressure of HF, have been studied by x-ray diffraction. They are orthorhombic, space group $P2_12_12_1$, with a = 8.52 ± 0.02, b = 11.09 ± 0.03, c = 6.69 ± 0.02 A. The unit cell contains eight formula units, and the calculated density is 2.06 g cm^{-3}. The structure corresponds to a salt of potassium and hydrogen-bonded ions $FHFHF^-$. Hydrogen-bond lengths in these ions average 2.33 A. The F-F-F angles are 130° and 139°, respectively, in the two nonequivalent $H_2F_3^-$ ions.

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Introduction

Alkali fluorides crystallize from HF solutions in the form of many solvates. For example, in the KF-HF system Cady (1934) observed the phases KF.HF, KF.2HF, 2KF.5HF, KF.3HF, and KF.4HF. It is well known that in KF.HF the fluorine atoms are connected in pairs by strong hydrogen bonds, and it is convenient to consider this substance as a salt of K^+ and HF_2^- ions. We speculated that in the higher solvates other polymeric ions occur: $FHFHF^-$, $FHFHFHF^-$, etc. By a determination of the crystal structure by x-ray diffraction, we have confirmed that in KF.2HF the fluorine atoms are grouped into $FHFHF^-$ ions, and consequently we write the formula as KH_2F_3.

The phase KH_2F_3 melts congruently at 71.7° (Cady, 1934). Because of an appreciable vapor pressure of HF, there was some difficulty in obtaining and photographing suitable crystals. The structure was determined by data from photographs of lower quality than we had hoped to obtain.

Crystals were prepared and photographed (by M. E. S.) in 1954, and the unit cell and space group were determined. The prospect of locating eight atoms in the asymmetric unit of a noncentric crystal with data of doubtful accuracy and with rather inadequate computing facilities was not as interesting as several other problems, and the work was suspended. In 1961 and 1962 the old photographs were examined again and were used to determine the structure which is reported here.

Experimental

Crystals of KH_2F_3 were prepared in a metal vacuum system. A weighed amount of anhydrous HF was allowed to enter an evacuated vessel containing the equivalent amount of reagent grade KF. The system was placed in boiling water for two hours to allow equilibration above the melting point of the product. When cooled and opened in a dry box, the vessel was found to contain a hard transparent mass which was crushed to yield single crystal fragments.

Crystals contained in polyethylene tubes were examined by x-ray diffraction at room temperature, about 24°. Weissenberg photographs were taken with copper radiation (λ = 1.5418 A for CuKα) with rotation about the c axis (layers 0 to 4) and about the a axis (layers 0 and 1). Unit cell dimensions were estimated from the two zero layer photographs. Intensities were estimated on the multiple film Weissenberg photographs (ℓ=0 to ℓ=4) by visual comparison with a standard film strip on which one reflection was exposed for various times. Intensities were recorded for 524 independent reflections, while 56 others were recorded as too weak to be observed. Lorentz, polarization and velocity corrections were applied. For CuKα radiation the absorption coefficient is estimated as 138 cm^{-1}, and the intensity data show severe effects of absorption. No absorption correction was made because the dimensions of the crystal are not known. The data from the five layers were placed on a common scale first according to the exposure times, but later the five scale factors were adjusted to improve the agreement of observed and calculated structure factors.

Unit Cell and Space Group

The diffraction patterns show orthorhombic symmetry with unit cell dimensions:

$$a = 8.52 \pm 0.02 \text{ A}$$

$$b = 11.09 \pm 0.03 \text{ A}$$

$$c = 6.69 \pm 0.02 \text{ A}.$$

Reflections are absent for h00 with h odd, for 0k0 with k odd, and for 00ℓ with ℓ odd. These absences correspond to space group $P2_12_12_1$ which is confirmed by the success of the structure determination. In this space group there is only one set of equivalent positions:

$$4(a) \quad x,y,z;\ \tfrac{1}{2} - x,\ \bar{y},\ \tfrac{1}{2} + z;\ \tfrac{1}{2} + x,\ \tfrac{1}{2} - y,\ \bar{z};\ \bar{x},\ \tfrac{1}{2} + y,\ \tfrac{1}{2} - z.$$

Therefore the number of formula units per unit cell must be divisible by 4. Ionic volumes in other crystals suggest that $8(KH_2F_3)$ is the only reasonable content of the unit cell. On this basis the calculated density is 2.06 g cm^{-3}.

Determination of the Structure

The asymmetric unit contains two potassium atoms and six fluorine atoms. The coordinates of the potassium atoms were determined uniquely from a three-dimensional Patterson function. We attempted to locate the fluorine atoms in projections (which are centric) based on the hk0 and h0ℓ data with phases determined only by potassium, but failed. The number of phases which could be determined was rather small, and the location of both potassium atoms at z=0 introduced extra symmetry.

The three-dimensional electron density function was calculated using phases calculated from the potassium atoms. This function was perplexing, but we identified four fluorine atoms by rejecting peaks which corresponded to unreasonably short interatomic distances and those for which we could not find K_1-F and K_2-F peaks in the Patterson function.

A second electron density function was calculated with phases determined by the two potassium atoms and the four fluorine atoms. With the same criteria, we were able to identify the remaining two fluorine atoms.

The structure was then refined by least squares. In all calculations we used the atomic scattering factors for K^+ and F^- from the tables of Ibers (1962). The calculations were made with an IBM-7090 computer and a full-matrix program written by P. K. Gantzel, R. A. Sparks and K. N. Trueblood, with minor changes. Each reflection was assigned unit weight. Each atom was assigned an individual isotropic temperature factor of the form $\exp(-B\lambda^{-2}\sin^2\theta)$.

Refinement with all the data made it evident that absorption errors were present. Refinement was continued with 551 reflections (of which 56 are zero) where $\sin\theta/\lambda$ exceeded 0.2. For these data the conventional reliability factor $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$ was reduced to 0.202 after 6 cycles.

The computer program used had no provision for refining the separate scale factors of the different layers, so these factors were adjusted by hand, and R fell to 0.186. Because the low angle data still seemed to be affected by absorption, further refinement was done with reflections for which $\sin\theta/\lambda$ exceeded 0.3 (487 terms of which 54 are zero). After further rescaling, R was reduced to 0.142. At this stage, shifts of coordinates were negligible. Including scale factors, a total of 37 parameters were used to achieve this fit.

Observed and calculated structure factors for all of the reflections which were measured are listed in Table 1. The calculated values are based on the coordinates and the first set of temperature parameters listed in Table 2. The standard deviations listed in Table 2 are those estimated by the method of least squares assuming that the discrepancies represent random errors.

It is expected that the higher angle data, on which the final parameters are based, include systematic errors due to absorption which are largely compensated by incorrect temperature parameters and scale factors. To the extent that such compensation occurs, the coordinates are not affected by these errors. A second set of temperature parameters, also listed in Table 2, were determined using only the data with $\ell=0$, and they are systematically greater than the first set. This result implies that further adjustment of the scale factors could improve the fit, but it was decided that the quality of the data did not justify further adjustment. Because of the uncertainty in the relative magnitudes of these thermal parameters, no correction of bond distances for thermal motion has been made. Such corrections are not expected to exceed 0.02 A for K-F distances or 0.01 A for F-F distances.

Discussion of the Structure

Fluorine atoms occur in the structure in groups of three as was expected for hydrogen-bonded $H_2F_3^-$ ions (Fig. 1). The two nonequivalent groups permit independent measurement of four hydrogen-bond distances and two bond angles which are listed in Table 3. These bond distances average 2.33 A, and the deviations from this average are of doubtful significance. The difference in the two bond angles is significant, and we infer that the molecule is not very rigid and that it bends to improve the crystal packing. This idea is consistent with the F-F-F angles reported for hydrogen fluoride. In the solid, HF occurs in zig-zag chains with angles of 120.1° (Atoji and Libscomb, 1954). In the gaseous polymer, the angle is observed as 144° by electron diffraction (Bauer, Beach and Simons, 1939).

Distances for hydrogen bonds between fluorine atoms in some other crystals are listed in Table 4. The bond lengths which we observe in KH_2F_3 are close to those observed in the FHF^- ion in various crystals, and they are significantly shorter than the bonds in solid hydrogen fluoride. On the basis of thermodynamic, spectral and dielectric data for KHF_2, Westrum and Pitzer (1949) concluded that the potential curve for the proton in the bifluoride ion has a single minimum at the midpoint. Peterson and Levy (1952) confirmed by neutron diffraction that in KHF_2 the hydrogen atoms are centrally located in the hydrogen bonds. Atoji and Lipscomb (1954) found evidence in their x-ray study of solid hydrogen fluoride that the hydrogen atoms are unsymmetrically located in these longer hydrogen bonds, as is generally accepted.

The distances which we observe for the hydrogen bonds in KH_2F_3 imply that these bonds approach in stability those in bifluoride ions. This fact suggests that the potential curve for the proton in one of these bonds may also be of the single-minimum type. The accuracy of our x-ray diffraction data does not permit us to test this conjecture, nor do we know of any other evidence which bears on the question. If such a minimum does occur, symmetry does not require it to be at the center of the bond.

The structure as a whole is salt like, with the potassium ions well dispersed among the $H_2F_3^-$ ions. The shortest potassium-potassium distance is 4.34 A. Each potassium atom has eight fluorine neighbors, each a member of a different $H_2F_3^-$ ion, at distances averaging 2.83 A for K_1 and 2.82 A for K_2.

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Table 1. Observed structure factors (FOB) and calculated structure factor magnitudes (FCAL) and phase angles (PHI) for KH_2F_3. Each structure factor has been multiplied by 10. Each term for which sin θ/λ is less than 0.3 was given zero weight and is marked with an asterisk (*).

L= 0

H	K	FOB	FCAL	PHI	H	K	FOB	FCAL	PHI	H	K	FOB	FCAL	PHI	H	K	FOB	FCAL	PHI	H	K	FOB	FCAL	PHI	H	K	FOB	FCAL	PHI
2	0	211	233	180*	4	2	503	567	180*	2	4	246	237	0*	0	6	0	3	180*	0	8	287	293	180	4	10	158	169	180
4	0	353	424	180*	5	2	88	51	90	3	4	284	297	270*	1	6	400	443	270*	1	8	421	407	270	5	10	156	166	270
6	0	393	347	180	6	2	131	113	180	4	4	522	597	0*	2	6	361	424	180*	2	8	449	498	0	6	10	76	91	180
8	0	519	521	0	7	2	348	271	270	5	4	218	175	270	3	6	193	187	270	3	8	379	389	90	7	10	139	161	90
10	0	57	65	0	8	2	231	208	180	6	4	221	208	0	4	6	366	320	0	4	8	375	331	180	1	11	141	166	90
1	1	106	128	270*	9	2	272	285	90	7	4	483	419	90	5	6	277	269	90	5	8	531	536	90	2	11	149	137	0
2	1	255	305	0*	10	2	135	114	0	8	4	249	228	180	6	6	218	179	180	6	8	92	71	0	3	11	269	303	270
3	1	641	1294	270*	1	3	360	497	270*	9	4	0	30	270	7	6	194	180	270	7	8	180	142	270	4	11	68	40	180
4	1	291	248	0*	2	3	304	314	0*	10	4	0	25	0	8	6	0	11	0	1	9	582	624	270	5	11	196	253	90
5	1	267	191	90*	3	3	376	480	90*	1	5	583	865	90*	9	6	0	3	270	2	9	361	384	180	0	12	189	222	0
6	1	503	471	180	4	3	288	231	0*	2	5	171	179	180*	1	7	111	118	270	3	9	0	17	270	1	12	194	243	90
7	1	358	321	90	5	3	328	286	270	3	5	263	238	90*	2	7	513	521	180	4	9	219	202	180	2	12	169	202	180
8	1	318	249	0	6	3	351	286	180	4	5	0	15	180	3	7	70	84	90	5	9	0	6	270	3	12	63	95	270
9	1	0	7	270	7	3	180	132	90	5	5	71	67	270	4	7	73	60	180	6	9	343	381	0	1	13	0	40	270
10	1	98	83	180	8	3	0	45	180	6	5	0	9	180	5	7	94	63	270	7	9	181	234	90	2	13	308	313	0
0	2	90	131	180*	9	3	137	144	270	7	5	464	438	270	6	7	0	33	180	0	10	310	288	0	3	13	167	151	90
1	2	164	204	90*	10	3	227	223	0	8	5	103	110	180	7	7	73	55	270	1	10	182	185	270	0	14	279	367	180
2	2	161	99	0*	0	4	293	759	180*	9	5	259	269	90	8	7	336	352	0	2	10	0	21	0					
3	2	319	358	270*	1	4	459	619	90*	10	5	175	170	0	9	7	74	108	90	3	10	0	47	90					

L= 1

H	K	FOB	FCAL	PHI	H	K	FOB	FCAL	PHI	H	K	FOB	FCAL	PHI	H	K	FOB	FCAL	PHI	H	K	FOB	FCAL	PHI	H	K	FOB	FCAL	PHI
2	0	331	419	90*	4	2	446	371	148*	3	4	580	766	177*	3	6	119	95	348	4	8	0	34	161	0	11	0	39	270
3	0	552	768	270*	5	2	372	319	95	4	4	437	443	15	4	6	256	224	259	5	8	400	377	201	1	11	97	107	148
4	0	269	271	270*	6	2	366	303	286	5	4	568	555	17	5	6	298	301	168	6	8	167	162	316	2	11	95	46	164
5	0	272	226	270	7	2	453	408	13	6	4	280	251	75	6	6	413	432	90	7	8	61	95	187	3	11	0	51	60
6	0	380	324	270	8	2	199	177	66	7	4	100	67	277	7	6	155	131	71	8	8	149	169	49	4	11	86	68	45
7	0	0	9	90	9	2	311	287	172	8	4	0	42	49	8	6	153	167	249	0	9	0	38	90	5	11	271	284	9
8	0	141	95	270	10	2	69	65	217	9	4	144	135	239	9	6	0	51	41	1	9	98	136	194	0	12	0	48	180
9	0	0	30	90	0	3	424	768	270*	10	4	228	237	271	0	7	410	388	90	2	9	171	240	34	1	12	333	365	169
10	0	469	496	90	1	3	50	100	196*	0	5	472	550	270*	1	7	205	184	17	3	9	187	212	339	2	12	216	200	84
2	1	277	327	255*	2	3	340	440	125*	1	5	318	334	12*	2	7	368	392	285	4	9	400	344	265	3	12	79	91	347
3	1	357	388	27*	3	3	318	303	35*	2	5	408	534	140*	3	7	258	241	143	5	9	119	122	61	4	12	50	100	333
4	1	620	687	84*	4	3	368	320	139*	3	5	506	564	158*	4	7	166	109	98	6	9	126	153	104	0	13	0	6	270
5	1	125	89	297	5	3	372	313	164	4	5	281	244	244	5	7	157	101	262	7	9	54	89	160	1	13	71	104	115
6	1	398	357	252	6	3	0	48	338	5	5	93	86	106	6	7	199	180	270	0	10	142	119	180	2	13	197	213	275
7	1	278	252	169	7	3	273	248	344	6	5	251	228	59	7	7	0	33	4	1	10	213	211	5	3	13	113	120	74
8	1	0	35	293	8	3	278	293	294	7	5	158	150	301	8	7	360	375	94	2	10	265	310	119	4	13	291	401	89
9	1	91	99	163	9	3	163	137	189	8	5	0	53	321	9	7	58	79	5	3	10	171	194	176	0	14	46	46	180
10	1	72	91	292	10	3	65	69	309	9	5	346	347	357	0	8	223	237	0	4	10	96	94	278	1	14	87	127	196
1	2	295	434	179*	0	4	314	436	180*	0	6	426	424	180*	1	8	92	69	9	5	10	218	220	347					
2	2	202	261	248*	1	4	556	811	300*	1	6	75	112	92*	2	8	115	116	338	6	10	200	175	247					
3	2	346	370	62*	2	4	381	369	285*	2	6	137	145	195	3	8	283	271	9	7	10	173	189	187					

L= 2

H	K	FOB	FCAL	PHI	H	K	FOB	FCAL	PHI	H	K	FOB	FCAL	PHI	H	K	FOB	FCAL	PHI	H	K	FOB	FCAL	PHI	H	K	FOB	FCAL	PHI
1	0	194	293	180*	0	2	132	210	0*	10	3	249	229	9	0	6	203	222	180	1	8	247	251	288	3	10	180	215	74
2	0	472	928	180*	1	2	451	1033	76*	0	4	443	630	180*	1	6	275	304	185	2	8	336	350	27	4	10	324	283	163
3	0	192	167	180*	2	2	365	543	44*	1	4	100	117	73*	2	6	278	258	154	3	8	0	40	358	5	10	139	137	292
4	0	61	75	0*	3	2	523	636	250*	2	4	142	162	180*	3	6	194	173	84	4	8	349	286	181	6	10	119	128	162
5	0	160	165	0	4	2	249	184	164*	3	4	204	214	234*	4	6	630	706	355	5	8	137	128	76	7	10	114	144	82
6	0	395	352	180	5	2	255	225	263	4	4	0	18	15	5	6	343	375	97	6	8	209	196	316	0	11	118	131	90
7	0	229	191	0	6	2	402	332	2	5	4	420	393	248	6	6	107	103	205	7	8	249	246	255	1	11	117	82	190
8	0	228	203	0	7	2	0	40	2	6	4	296	264	76	7	6	132	139	270	8	8	56	93	159	2	11	236	218	339
9	0	188	193	180	8	2	60	57	15	7	4	123	118	100	8	6	73	45	162	9	8	22	117	302	3	11	519	457	276
10	0	0	80	180	9	2	437	401	85	8	4	284	248	222	9	6	0	13	50	0	9	86	48	270	4	11	0	41	101
0	1	105	172	270*	10	2	78	156	314	9	4	181	150	319	0	7	130	122	90	1	9	424	435	255	5	11	347	324	89
1	1	141	236	71*	0	3	375	653	270*	0	5	158	201	90*	1	7	120	103	67	2	9	87	78	95	0	12	265	303	0
2	1	290	393	10*	1	3	227	329	244*	1	5	481	582	96*	2	7	433	479	192	3	9	87	94	29	1	12	126	154	126
3	1	418	455	243*	2	3	456	709	9*	2	5	242	239	267*	3	7	238	242	100	4	9	86	90	137	2	12	70	90	189
4	1	373	386	10*	3	3	453	539	111*	3	5	122	109	93	4	7	171	149	349	5	9	101	118	313	3	12	195	193	271
5	1	338	305	86	4	3	271	235	17	4	5	0	21	258	5	7	107	109	270	6	9	230	210	354	4	12	57	86	82
6	1	447	434	182	5	3	396	339	299	5	5	194	194	34	6	7	86	85	20	7	9	219	236	103	5	12	128	128	284
7	1	221	215	18	6	3	435	389	169	6	5	151	127	51	7	7	158	166	285	8	9	135	178	230	0	13	0	42	270
8	1	136	109	5	7	3	195	170	75	7	5	345	373	254	8	7	209	187	358	0	10	370	400	0	1	13	57	69	295
9	1	76	112	259	8	3	206	125	193	8	5	167	171	116	9	7	121	128	146	1	10	87	99	128	2	13	141	156	14
10	1	81	93	242	9	3	192	136	299	9	5	199	183	73	0	8	347	345	180	2	10	0	11	273	3	13	90	112	114

L= 3

H	K	FOB	FCAL	PHI	H	K	FOB	FCAL	PHI	H	K	FOB	FCAL	PHI	H	K	FOB	FCAL	PHI	H	K	FOB	FCAL	PHI	H	K	FOB	FCAL	PHI
1	0	282	604	90*	10	1	148	138	262	9	3	219	176	152	9	5	294	307	13	1	8	79	60	337	5	10	209	178	306
2	0	286	377	90*	0	2	304	761	180*	0	4	196	252	180*	0	6	285	311	0	2	8	80	66	88	6	10	165	165	269
3	0	0	69	270*	1	2	346	681	181*	1	4	323	463	7*	1	6	255	258	278	3	8	362	360	27	0	11	194	118	270
4	0	0	61	90	2	2	268	365	59*	2	4	154	173	218	2	6	378	430	318	4	8	228	238	170	1	11	224	181	144
5	0	173	177	90	3	2	235	261	266*	3	4	327	356	159	3	6	342	304	8	5	8	221	196	211	2	11	141	134	21
6	0	78	49	270	4	2	287	287	42	4	4	159	117	39	4	6	200	201	202	6	8	160	199	247	3	11	47	99	5
7	0	81	91	270	5	2	205	220	304	5	4	318	300	22	5	6	222	173	150	7	8	128	135	150	4	11	42	81	51
8	0	363	296	270	6	2	374	365	307	6	4	229	209	144	6	6	427	432	92	8	8	181	160	96	5	11	258	238	3
9	0	161	167	90	7	2	334	343	345	7	4	80	101	126	7	6	91	92	239	0	9	0	43	90	0	12	139	139	180
10	0	306	322	90	8	2	132	135	131	8	4	0	43	58	8	6	219	212	299	1	9	81	90	130	1	12	321	309	175
0	1	156	322	90*	9	2	318	291	190	9	4	0	35	22	0	7	659	785	90	2	9	298	283	41	2	12	82	71	116
1	1	248	451	176*	0	3	261	449	270*	0	5	254	299	270	1	7	268	330	282	3	9	150	163	311	3	12	91	102	297
2	1	280	413	280*	1	3	87	122	101*	1	5	162	241	310	2	7	275	268	249	4	9	305	291	262	0	13	88	67	90
3	1	416	554	59*	2	3	161	239	58*	2	5	335	358	125	3	7	158	134	218	5	9	72	67	68	1	13	0	32	30
4	1	426	446	47	3	3	328	350	101	3	5	291	277	221	4	7	214	164	233	6	9	63	51	61	2	13	165	182	254
5	1	392	378	330	4	3	269	245	96	4	5	198	157	246	5	7	181	110	232	0	10	178	167	0					
6	1	207	223	228	5	3	218	179	186	5	5	138	89	87	6	7	278	247	308	1	10	307	356	25					
7	1	263	204	203	6	3	80	34	150	6	5	81	65	10	7	7	153	167	79	2	10	253	255	107					
8	1	0	21	59	7	3	383	385	331	7	5	0	23	255	8	7	362	342	92	3	10	92	108	207					
9	1	65	67	183	8	3	316	260	255	8	5	127	145	303	0	8	79	46	0	4	10	187	190	347					

L= 4

H	K	FOB	FCAL	PHI	H	K	FOB	FCAL	PHI	H	K	FOB	FCAL	PHI	H	K	FOB	FCAL	PHI	H	K	FOB	FCAL	PHI	H	K	FOB	FCAL	PHI
1	0	62	90	0	9	1	123	87	256	7	3	87	80	44	6	5	125	87	258	6	7	113	93	6	0	10	252	223	0
2	0	146	126	180	0	2	142	222	180	8	3	0	31	170	7	5	360	306	249	7	7	169	102	189	1	10	250	233	228
3	0	272	292	0	1	2	152	249	26	9	3	189	141	358	8	5	207	174	123	8	7	126	121	9	2	10	81	64	142
4	0	75	79	0	2	2	165	213	282	0	4	184	247	180	0	6	81	63	180	0	8	0	50	180	3	10	54	95	104
5	0	0	31	180	3	2	302	334	253	1	4	164	161	59	1	6	82	100	228	1	8	90	74	292	4	10	110	119	201
6	0	180	173	180	4	2	371	397	172	2	4	168	164	24	2	6	305	264	186	2	8	181	206	352	5	10	143	103	315
7	0	199	163	0	5	2	211	205	351	3	4	96	110	88	3	6	278	297	343	3	8	156	187	110	0	11	0	13	270
8	0	440	411	0	6	2	239	203	72	4	4	365	357	322	4	6	361	401	343	4	8	261	282	188	1	11	0	73	69
9	0	225	211	180	7	2	0	43	127	5	4	269	205	259	5	6	291	250	178	5	8	335	310	59	2	11	208	154	313
0	1	31	8	90	8	2	78	48	147	6	4	270	243	59	6	6	233	216	195	6	8	256	200	323	3	11	296	275	264
1	1	111	169	252	9	2	157	222	111	7	4	267	254	110	7	6	224	156	256	7	8	187	152	231	4	11	274	252	96
2	1	156	202	127	0	3	0	51	270	8	4	237	187	203	8	6	144	118	150	0	9	0	49	270	0	12	179	126	0
3	1	299	369	265	1	3	159	215	334	0	5	180	224	90	0	7	195	194	90	1	9	219	226	275	1	12	276	220	117
4	1	170	141	40	2	3	286	336	44	1	5	371	425	67	1	7	0	12	100	2	9	197	166	163	2	12	172	181	231
5	1	318	331	107	3	3	420	501	118	2	5	294	313	320	2	7	267	313	186	3	9	85	75	69					
6	1	285	285	231	4	3	315	278	258	3	5	221	185	190	3	7	128	176	4	4	9	80	94	211					
7	1	141	135	51	5	3	378	363	273	4	5	125	78	171	4	7	180	140	345	5	9	72	71	290					
8	1	160	135	328	6	3	240	196	143	5	5	0	42	19	5	7	87	38	212	6	9	227	237	17					

Table 2.

Final atomic parameters for KH_2F_3.

	x	y	z	σ(x)	σ(y)	σ(z)	B in A^2 (1)	B in A^2 (2)
K_1	0.2317	0.1789	0.0219	0.0004	0.0003	0.0009	0.7	1.4
K_2	0.1224	0.5974	0.0217	0.0004	0.0003	0.0010	0.7	1.3
F_1	0.3582	0.1737	0.6544	0.0013	0.0010	0.0025	1.3	1.9
F_2	0.1989	0.0629	0.4338	0.0015	0.0011	0.0027	1.7	2.4
F_3	0.1154	0.3625	0.2402	0.0016	0.0012	0.0030	2.2	2.6
F_4	0.0877	0.4681	0.6874	0.0017	0.0014	0.0031	2.5	3.0
F_5	0.5022	0.2229	0.2415	0.0016	0.0012	0.0034	1.9	2.6
F_6	0.4195	0.3929	0.9246	0.0016	0.0012	0.0030	2.0	3.3

Table 3. Interatomic distances and angles in KH_2F_3.

F_1-F_2	2.35 A	F_2-F_1-F_3	130 ± 2°
F_1-F_3	2.34		
F_4-F_5	2.29	F_5-F_4-F_6	139 ± 2°
F_4-F_6	2.34		
K_1-F_1	2.69	K_2-F_4	2.67 A
K_1-F_3	2.69	K_2-F_1	2.69
K_1-F_5	2.78	K_2-F_6	2.72
K_1-F_6	2.80	K_2-F_2	2.78
K_1-F_2	2.81	K_2-F_4	2.80
K_1-F_5	2.85	K_2-F_5	2.94
K_1-F_6	2.94	K_2-F_3	2.96
K_1-F_2	3.05	K_2-F_3	2.99

The standard deviation of each distance is 0.02 A.

Table 4. Distances for F-H-F bonds in various crystals.

Crystal	Average Distance
HF (Atoji and Lipscomb, 1954)	2.49 ± 0.01 A
KHF_2 (Helmholz and Rogers, 1939)	2.26 ± 0.01
NH_4HF_2 (Helmholz and Rogers, 1940)	2.32 ± 0.03
$LiHF_2$ (Frevel and Rinn, 1962)	2.27 ± 0.11
KH_2F_3 (Present work)	2.33 ± 0.01

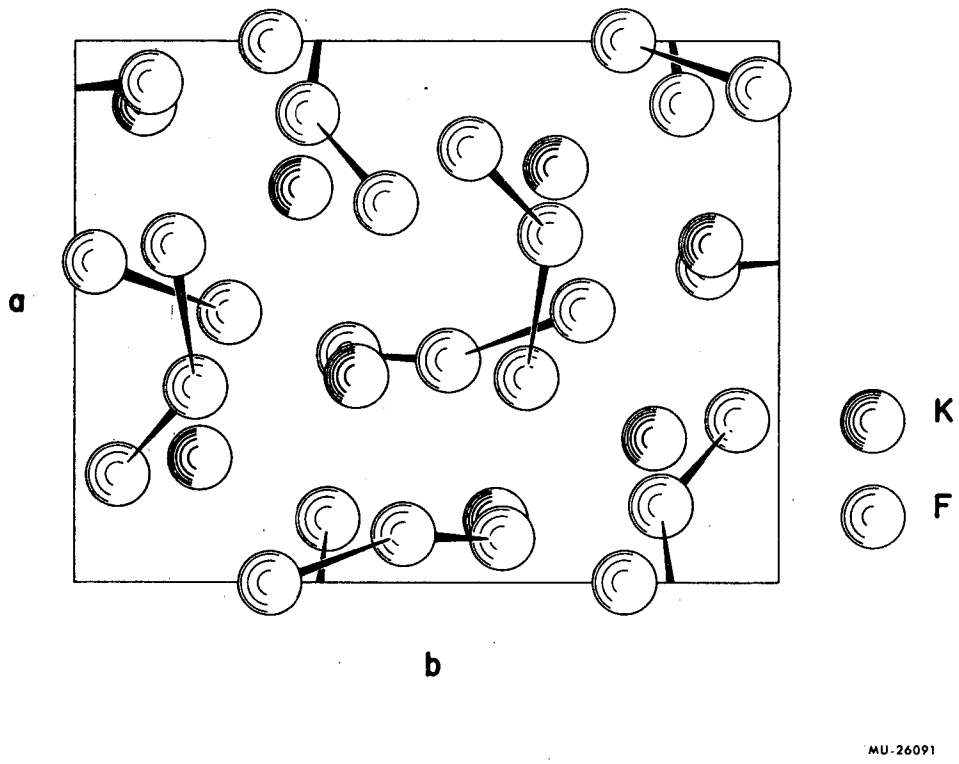

Fig. 1. Crystal structure of KH_2F_3, projected along c.

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