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ELECTRON DIFFRACTION STUDY OF THE STRUCTURE OF AMMONIUM SULFATE

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The structure of $(NH_4)_2SO_4$ has been studied by electron diffraction. The study was carried out on the basis of intensities determined from electron diffraction spot patterns. A dynamic correction was introduced for the intensities. Cross sections of three-dimensional Fourier syntheses were constructed in the planes $y = {}^1/_4$ and $y = {}^3/_{60}$. Sections were also constructed from difference Fourier series in the planes $y = {}^1/_4$ and $y = {}^6/_{60}$. From these syntheses the coordinates of all atoms, including H, have been determined. The reliability coefficient is 36%. Interatomic distances are calculated, and it is shown that the SO_4 and NH_4 tetrahedra are strongly distorted. A possible explanation of this is the presence of hydrogen bonds in the structure.

Introduction

In 1956 it was discovered [1] that below −50°C ammonium sulfate exhibits ferroelectric properties.

A study of the crystallographic and structural features of the phase transformation from the paraelectric to the ferroelectric state would help to elucidate the role of structural changes in the formation of ferroelectric properties. At present it is assumed that the origin of the spontaneous polarization in crystals containing hydrogen is a function of a system of hydrogen bonds and depends upon the existence of ions with tetrahedral, pyramidal, or planar configurations.

Although the structure of $(NH_4)_2SO_4$ at room temperature was studied by x-ray techniques as early as 1916-1930 [2-6], nevertheless there are discrepancies in the structural data. Furthermore, in these papers the parameters of hydrogen were not determined. The problem in this present work consisted in a correction of the general structure of the $(NH_4)_2SO_4$ model and in a localization of the hydrogen atoms using electron diffraction at room temperature. Because of peculiarities of the crystallization of ammonium sulfate, the electron diffraction study of its structure had to be carried out using electron diffraction spot patterns.

In the light of the contemporary dynamic theory of scattering of electrons, electron diffraction spot patterns are regarded as an example of a rather complex diffraction pattern which does not lead itself to a simple interpretation [7-10]. However, as the experience of structural analysis [11-13] shows, in particular the results of the present work, spot patterns from a mosaic single crystal can be used successfully in the solution of such delicate problems as the localization of hydrogen atoms in the presence of sulfur atoms, where the ratio of atomic number is 16:1. Apparently the block structure of a mosaic sample creates favorable conditions for kinematic scattering. An essential detail, not considered by theorists, appears to be that in electron diffraction spot patterns of a mosaic single crystal, each crystal particle as a rule participates in the formation of one reflection only. This probably explains the fact that a strongly expressed extinction effect for intense reflections is added to the Blackman correction in the approximation of two strong beams. At the same time a significant reduction in the coefficient of reliability is achieved.

Structural Data

According to the x-ray data [2-6], ammonium sulfate has an orthorhombic lattice with periods a = 5.97, b = 10.60, c = 7.76 A. The number of molecules Z = 4, and the space group is D_{2h}^{16} – Pmcn. The crystal belongs to the K_2SO_4 or Hl_6 structure type {according to the Strukturberichte classification [14] (see Fig. 6)}. The S atoms, half of the O atoms, and the NH_4 groups lie on symmetry planes and occupy the fourfold position c̲. Two O atoms occupy a general eighfold d̲ position. The parameters of all heavy atoms were determined from geometrical and crystal chemical considerations on the basis of the known pattern of K_2SO_4 [14]. It must be pointed out that the parameters of atoms which were de-

TABLE 1. Atomic Coordinates in the Structure of $(NH_4)_2SO_4$

Atom	Coordinates	[3]	[6]	Present work		Atom	Coordinates	[3]	[6]	Present work	
				1	2					1	2
S	x	0.250	0.252	0.254	0.256	H_I	x			0.045	0.044
	y	0.250	0.250	0.250	0.250		y			0.250	0.250
	z	0.417	0.420	0.419	0.420		z			0.072	0.059
O_I	x	0.056	0.053	0.046	0.045	H_{II}	x			0.158	0.147
	y	0.250	0.250	0.250	0.250		y			0.250	0.250
	z	0.417	0.411	0.415	0.409		z			0.200	0.193
O_{II}	x	0.315	0.311	0.311	0.308	H_{III}	x			0.384	0.380
	y	0.250	0.250	0.250	0.250		y			0.250	0.250
	z	0.549	0.544	0.545	0.540		z			0.720	0.720
O_{III}	x	0.315	0.311		0.317	H_{IV}	x			0.147	0.138
	y	0.045	0.045		0.041		y			0.250	0.250
	z	0.351	0.345		0.352		z			0.700	0.700
N_I	x	0.185	0.180	0.188	0.192	H_V	x				0.258
	y	0.250	0.250	0.250	0.250		y				0.111
	z	0.083	0.087	0.092	0.097		z				0.063
N_{II}	x	0.500	0.499	0.490	0.480	H_{VI}	x				0.457
	y	0.250	0.250	0.250	0.250		y				0.111
	z	0.811	0.778	0.810	0.805		z				0.861

Note: 1) Determined from the synthesis of Fig. 3; 2) determined from the syntheses of Figs. 4a, 4b and Figs. 5a, 5b.

termined by Ogg [3] and Taylor [6] do not coincide. The great difference in the atomic coordinates in these papers, visible at a glance, is explained by the fact that the coordinate origin chosen by Taylor is displaced relative to the origin of Ogg's cell along the X axis by 0.500 and along the Y axis by −0.500. After a reduction of the data to one system, the difference in atomic coordinates is 0.001-0.006 parts of the cell period (0.01-0.06 A). One exception is the atom N_{II} whose z parameter differs in the two papers by 0.033 (~ 0.3 A).

In the works cited, a setting was selected with a < c < b. We transformed the setting in our work to b < a < c, which is the setting accepted in the International Tables. In addition, as origins we chose atoms other N_I and N_{II} atoms. After insertion of the appropriate changes, the data regarding the atomic coordinates, as determined by x-ray methods, are presented in Table 1.

Methods of Study

The samples for study were prepared by crystallization of droplets of an aqueous solution of $(NH_4)_2SO_4$ with a concentration of 0.1-0.2%. They crystallized on an amorphous film at room temperature; occassionally the

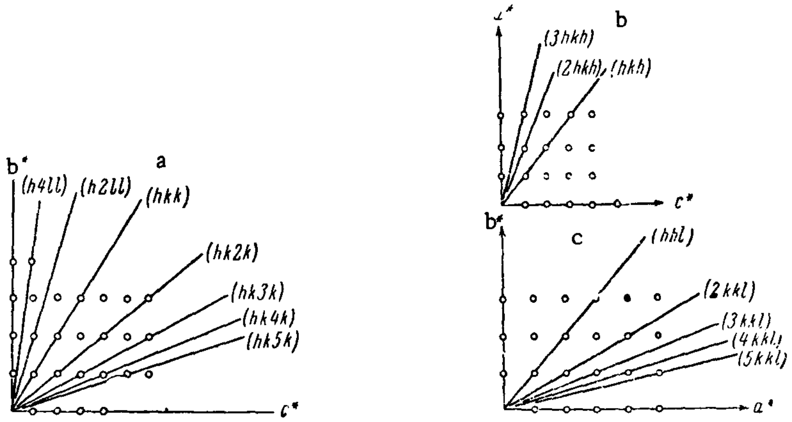

Fig. 1. Traces of the reciprocal lattice planes obtained by the rotation method: a) rotation about the a* axis; b) rotation about the b* axis; c) rotation about the c* axis.

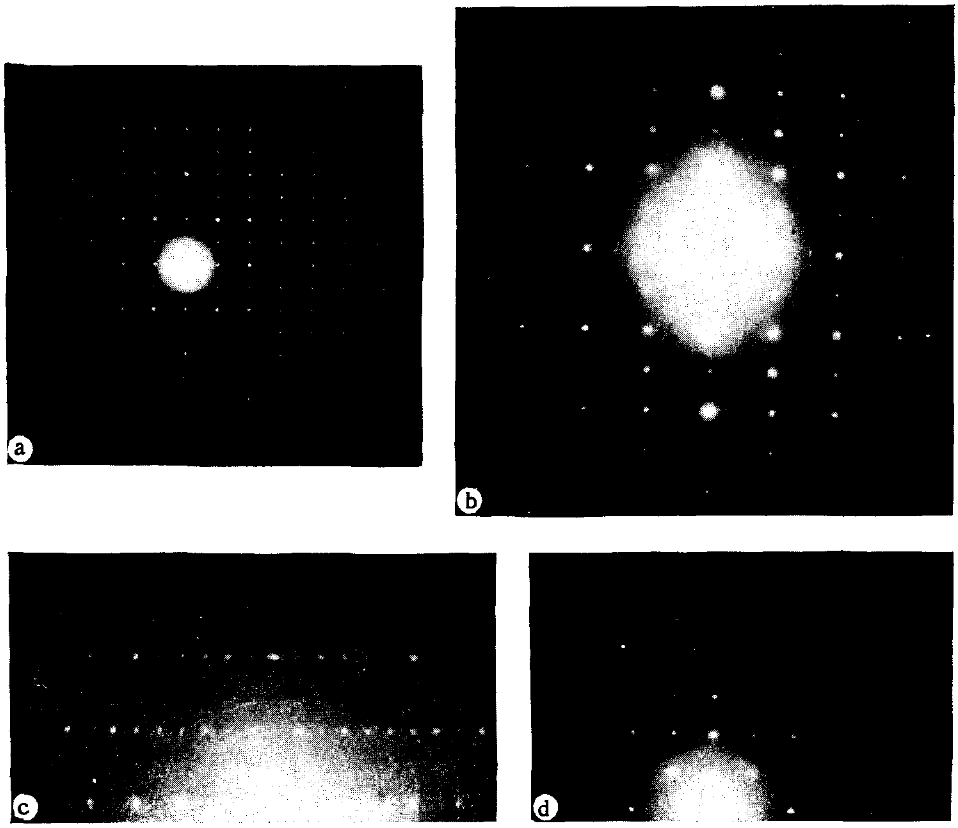

Fig. 2. Electron diffraction patterns of planes. a) h0l; b) 0kl;; c) hkh; d) 2kk$l$.

solution drops were placed on a substrate warmed to ~50°C. From these samples we obtained electron diffraction spot patterns.* In order to obtain a large number of reflections we used the rotation method [15]. Figure 1 shows the disposition of 18 planes of the reciprocal lattice which we succeeded in photographing. Some electron diffraction patterns are shown in Fig. 2. For all the planes of the reciprocal lattice we obtained electron diffraction patterns with multiple exposures. In the first stage of the study, estimation of the reflection intensities was carried out generally according to a 9-point scale. The experimental structure factors thus obtained were compared with theoretical values calculated without allowance for the scattering of hydrogen, and were also used in calculating a cross section of the F-series in the plane $y = {}^1\!/_4$. At the same time we observed a significant discrepancy between F_e and F_t and in the F-series section we secured only heavy atom peaks and strong parasitic maxima. Therefore we again estimated the reflection intensities according to x-ray darkening marks on the film, on a scale of 39 points.

A particular difficulty in the present case was the establishment of a single scale of intensities for all the electron diffraction patterns. We selected as the basis of our scale the intensities of the (h0l) reflections, of which there are 203. These intensities, however, as was also the case for all the other planes, were determined from multiple exposure electron diffraction patterns. Then, by comparison of the same reflections, which were available on different planes, we arrived at a mean coefficient of conversion of intensities to one scale. In this manner we obtained intensities for all 639 reflections (the range of intensities is from 6300 to 1 in relative units).

Determination of the intensities of the electron diffraction spot patterns using the method of scanning analysis proposed by Cowley [16] is practically impossible for such a large number of reflections. For conversion from intensities to structure factors we used the well-known formula $F_{hkl} = \sqrt{I/d_{hkl}}$. However, it is only natural to assume that electron diffraction spot patterns do not correspond to a case of pure kinematic scattering. Comparison of theoretical and experimental structure factors (Table 2) revealed a regular diminution of the experimental intensities for the strongest reflections. Therefore we introduced a dynamic correction for the strongest reflections [17]. In spite of the rather large scatter of the effective dimensions of the crystal particles (from 84 to 615 A, with a mean value

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*Electron diffraction patterns of polycrystalline samples and of textures which we succeeded in obtaining were of poor quality and it was not possible to use them in evaluating the reflection intensities.

TABLE 2. Theoretical and Experimental Structure Factors of the (h0*l*) Zone

Numerical order	*h0l*	F_t	F_e	Numerical order	*h0l*	F_t	F_e
1	101	0.07	0.32	291	509	0.08	0.13
2	022	1.06	1.00	293	2011	0.07	0.14
4	102	1.54	1.87	294	803	0.11	0.30
6	200	2.64	2.26	301	4011	0.08	0.17
7	201	0.19	0.33	304	608	0.08	0.18
10	103	0.47	0.49	314	804	0.17	0.19
11	202	1.54	2.20	317	3011	0.02	0.13
18	004	1.75	2.46	321	707	0.03	0.14
19	203	0.59	0.46	332	805	0.08	0.20
21	301	2.53	2.11	333	0012	0.12	0.17
22	104	0.35	0.28	339	1012	0.09	0.15
26	302	0.32	0.44	340	5010	0.14	0.14
30	204	0.62	0.59	345	609	0.10	0.13
33	303	1.25	1.45	352	4011	0.09	0.14
35	105	0.18	0.30	354	2012	0.08	0.15
41	400	1.86	2.38	355	901	0.04	0.17
45	401	1.06	1.33	361	902	0.22	0.20
47	205	0.77	0.69	363	806	0.16	0.15
48	304	0.13	0.59	365	708	0.17	0.13
51	402	0.63	0.70	379	903	0.11	0.14
56	006	0.47	0.63	381	3012	0.05	0.10
61	106	0.60	0.69	394	400	0.33	0.17
62	403	0.13	0.35	397	6010	0.07	0.11
67	305	0.14	0.40	399	5011	0.05	0.11
70	206	0.35	0.67	402	807	0.08	0.15
75	404	0.39	0.35	409	1013	0.04	0.09
80	501	0.95	1.16	411	709	0.04	0.09
86	502	0.85	0.74	413	4012	0.09	0.15
88	107	0.22	0.33	416	905	0.12	0.15
91	306	0.19	0.30	417	2013	0.03	0.09
98	405	0.71	0.57	430	808	0.11	0.12
99	503	0.19	0.45	434	3013	0.02	0.10
103	207	0.09	0.26	435	1000	0.04	0.19
115	504	0.51	0.40	438	906	0.11	0.14
117	008	0.37	0.33	439	1001	0.12	0.14
120	307	0.04	0.29	440	6001	0.05	0.10
121	406	0.41	0.50	449	1002	0.10	0.14
122	108	0.05	0.28	452	5012	0.06	0.13
126	600	0.38	0.34	453	7010	0.03	0.10
128	601	0.27	0.60	458	1003	0.07	0.14
137	602	0.47	0.45	462	0014	0.05	0.12
140	505	0.32	0.31	464	1014	0.06	0.09
141	208	0.16	0.30	467	4013	0.07	0.08
149	603	0.38	0.35	471	907	0.08	0.09
159	407	0.08	0.27	472	809	0.08	0.07
160	308	0.09	0.36	480	1004	0.05	0.10
166	506	0.13	0.26	483	2014	0.05	0.08
167	109	0.06	0.21	496	6012	0.07	0.09
168	604	0.07	0.26	498	1005	0.15	0.11
184	209	0.17	0.23	501	7011	0.04	0.07
190	605	0.32	0.27	502	3014	0.04	0.09
191	701	0.32	0.32	508	908	0.15	0.10
193	408	0.24	0.37	509	5013	0.04	0.07
197	702	0.14	0.22	515	8010	0.09	0.07
201	507	0.14	0.23	519	1006	0.18	0.11
207	309	0.10	0.24	525	4014	0.03	0.07
212	0010	0.11	0.15	527	1101	0.14	0.12
214	703	0.12	0.20	528	1015	0.02	0.07
218	1010	0.15	0.19	531	1102	0.10	0.13
219	606	0.46	0.22	535	909	0.03	0.06
231	704	0.57	0.34	536	2015	0.04	0.06
232	2010	0.17	0.23	539	1103	0.07	0.07
237	507	0.32	0.25	540	1107	0.04	0.07
240	409	0.08	0.17	541	7012	0.02	0.05
254	607	0.07	0.23	545	6013	0.02	0.06
255	705	0.06	0.22	552	8011	0.04	0.05
258	3010	0.09	0.18	554	1104	0.19	0.08
263	800	0.26	0.26	557	3015	0.02	0.06
269	801	0.16	0.18	558	5014	0.04	0.06
276	1011	0.10	0.16	561	1105	0.04	0.08
277	802	0.16	0.25	562	1008	0.05	0.07
290	706	0.17	0.16	564	9010	0.08	0.06

TABLE 2. (continued)

Numerical order	*h0l*	F_t	F_e	Numerical order	*h0l*	F_t	F_e
567	4015	0.03	0.06	608	6015	0.01	0.04
569	0016	0.07	0.05	609	1205	0.09	0.05
570	1016	0.05	0.05	610	9012	0.03	0.04
572	7013	0.02	0.07	614	5016	0.03	0.04
574	1106	0.03	0.07	615	1206	0.03	0.05
576	8012	0.03	0.07	616	1109	0.01	0.04
577	2016	0.02	0.07	617	10011	0.02	0.04
578	6014	0.03	0.05	618	1301	0.03	0.05
582	1009	0.04	0.05	619	7015	0.02	0.04
583	1200	0.07	0.11	621	1207	0.00	0.03
585	1201	0.04	0.07	623	1302	0.09	0.05
587	5015	0.01	0.04	626	1303	0.03	0.01
589	9011	0.03	0.05	628	11010	0.04	0,03
591	1202	0.06	0,07	629	1304	0.01	0,04
592	3016	0.03	0,07	630	1208	0.03	0.04
595	1107	0.05	0.06	632	1305	0.03	0,05
597	1203	0.04	0.07	633	1306	0.02	0.04
601	1204	0.03	0.05	634	1400	0.12	0.04
603	4016	0.02	0.05	635	1401	0.00	0.03
604	10010	0.05	0.05	636	1402	0.04	0.03
605	7014	0.02	0.04	637	1403	0.07	0,04
606	8013	0.02	0.03	638	1404	0.06	0.03
607	1108	0.06	0.06				

of 242 A), this approach gave a good result. Use of the method described in [18] for determination of the empirical scattering law is in this case less convenient because there are many reflections of great intensity.

For refinement of the coordinates of the H atoms we constructed difference Fourier syntheses. In their construction one generally uses structure factors which have been obtained according to the formula $F^H = F_e - F_t$, where F_t is calculated for all atoms with the exception of the H atom. The fundamental defect of this method is that all errors in the determination of intensities enter into the difference synthesis. At the same time their weight increases because the value which is being determined is smaller than the magnitude of the usual synthesis. Therefore it is preferable to use the method proposed in [19] in which for the calculations one uses structure factors which are determined from the formula $F_e^H = (F_t^H/F_t) \cdot F_e$. And although the first of these methods possesses great objectivity, in this case it is possible to use the second method because the coordinates of the H atoms were first determined from a typical Fourier synthesis calculated from the signs of the structure factors determined on the basis of a model involving the heavy atoms.

In the calculation of the theoretical structure factors we used atomic factors, according to [20]. We introduced an isotropic temperature correction in deriving the theoretical structure factors ($B_S = 1.2$, $B_O = B_N = 2$, $B_H = 2.7$).

Course of the Study

Study of the systematic extinctions in the electron diffraction patterns of $(NH_4)_2SO_4$ indicated that systematic absences occur for hk0 reflections for which h $\neq$ 2n and for (0k*l*) reflections for which k + *l* $\neq$ 2n†, corresponding to the space group D_{2h}^{16}–Pnma or C_{2v}^{9}–Pn2a. Analysis of the physical properties of ammonium sulfate at room temperature enables one to select the space group D_{2h}^{16}–Pnma, which is found to be in agreement with the x-ray data [2-6].

As was pointed out above, in agreement with the x-ray data, $(NH_4)_2SO_4$ belongs to the K_2SO_4 structure type. In this structure type a large part of the atoms are situated on a symmetry plane, and therefore the most characteristic feature of the structure is a section of the potential in the plane y = ¼.

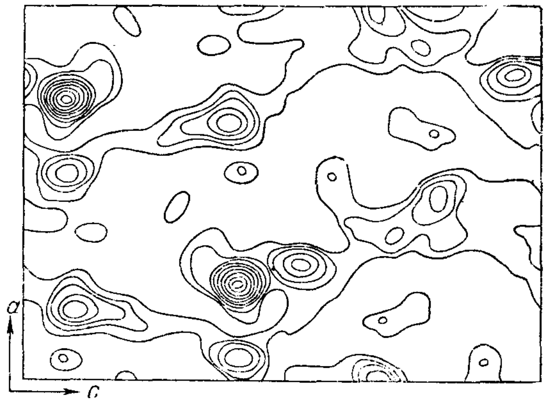

Fig. 3. Section in the plane y = ¼ in relative units.

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† It must be pointed out that in some of the hk0 and 0k*l* electron diffraction patterns forbidden reflections are present. However, the determination of intensities was made for those electron diffraction patterns in which the extinction rules are obeyed.

Since we had at our disposal two structure models established by x-ray techniques [3, 6], we then also calculated the signs of the structure factors on the basis of these two models, using only the heavy atoms. The section in the plane $y = {}^{1}/_{4}$, calculated according to the signs in Ogg's structure, is shown in Fig. 3. This section is of interest in two respects.

1. The coordinates of the heavy atoms which are obtained from it agree, with a precision of thousandths of a cell parameter, with the coordinates provided by the x-ray data.

2. Maximas and steps close to the N atoms which lie on the plane of symmetry are clearly evident; these correspond to hydrogen atoms. The heights of these maxima significantly exceed the heights of parasitic maxima in this section. The reliability coefficient (after introduction of a dynamic correction) in this case is 42.0% (for Ogg's model) and 44.7%(for Taylor's model).

The coordinates of the S, O_{I}, O_{II}, N_{I}, N_{II}, H_{I}, H_{II}, H_{III}, and H_{IV} atoms were determined from that section with the aid of strips along the X and Z axes through the maximum values of the peak heights. The atomic coordinates of the atoms H_{V} and H_{VI} were calculated on the basis of a model of the NH_4 ion in the form of a regular tetrahedron with an N–H distance of 1 A, and an H–N–H angle equal to 109°30'.

On the basis of these data, now including calculations of the hydrogen atom positions, we once again estimated the theoretical structure factors The signs of 48, i.e., 7.5%, of the structure factors were changed. We introduced a dynamic correction to 61 of the experimental structure factor values. We subsequently again calculated sections of the potential along the planes $y = {}^{1}/_{4}$ and $y = {}^{3}/_{60}$ (Fig. 4). In the section $y = {}^{3}/_{60}$ (Fig. 4b) the O_{III} atom is clearly visible. Furthermore, there is a maximum here which corresponds to the other O_{III} atom lying at $y = -0.041$; for refinement of the $\underline{y}$ coordinates of O_{III} we constructed strips along a straight line which passed through $x = 0.317$ and $z = 0.352$.

For more precise localization of the H atoms we constructed difference synthesis sections on $y = {}^{1}/_{4}$ and $y = {}^{6}/_{60}$ (Fig. 5). The atomic coordinates which we established from these sections are shown in Table 1. The root-mean-square error in the determination of coordinates calculated according to [21] is 0.004 for S, 0.01 for O, 0.01 for N, and 0.04 A for H. These values are probably on the low side. With a mean inner potential of 8.7 V, the heights of the potential maxima are $\varphi_S(0) = 379$ V, $\varphi_N(0) = 164$ V, $\varphi_O(0) = 158$ V, $\varphi_H(0) = 47$ V. The discrepancy in the values of $\varphi(0)$ for identical but

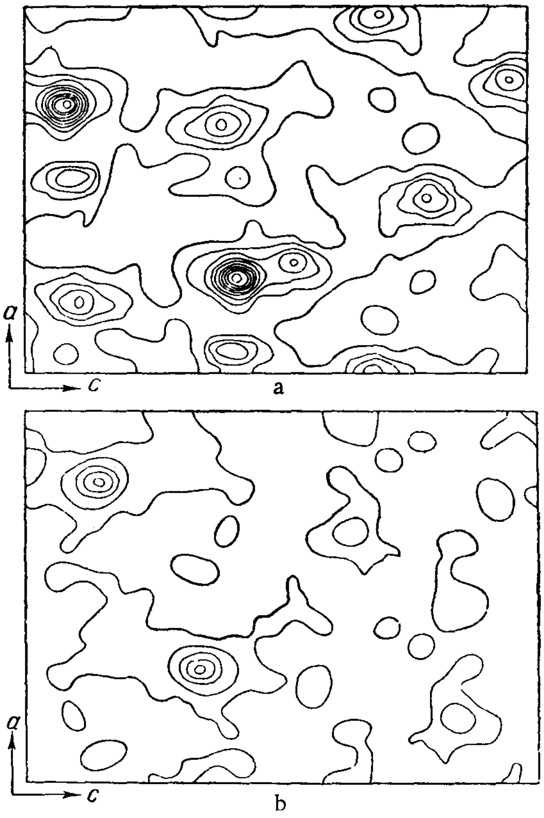

Fig. 4. Sections of the potential: a) along the plane $y = {}^{1}/_{4}$, and b) in the plane $y = {}^{3}/_{60}$. (The structure contours are at 8-V intervals.)

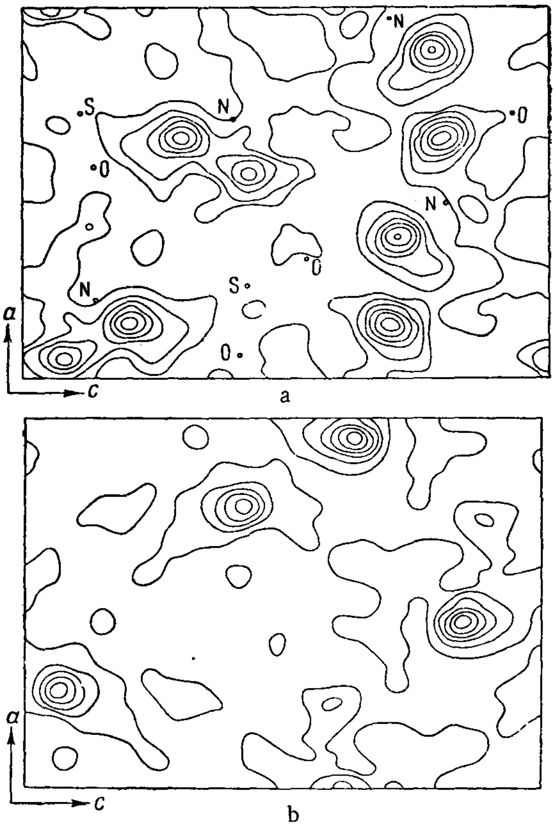

Fig. 5. Sections of the potential three-dimensional difference series: a) in the plane $y = {}^{1}/_{4}$, and b) in the plane $y = {}^{6}/_{60}$. (The structure contours are at 8-V intervals.)

TABLE 3. Interatomic Distances in Tetrahedra (in A)

Tetrahedra	Distance		Angles	
SO_4	$S-O_I$	1.61	O_I-S-O_{II}	111,° 6′
	(2) $S-O_{III}$	1.34	(2) O_I-S-O_{III}	104° 21′
	(2) $S-O_{III}$	1.51	(2) $O_{II}-S-O_{III}$	108° 41′
	mean	1.49	mean	108°1′
$(NH_4)_I$	N_I-H_I	1.15	$H_I-N_I-H_{II}$	94°25′
	N_I-H_{II}	1.07	(2) $H_I-N_I-H_V$	115°25′
	(2) N_I-H_V	1.03	(2) $H_{II}-N_I-H_V$	119°5′
	mean	1.08	mean	109°39′
$(NH_4)_{II}$	$N_{II}-H_{III}$	1.18	$H_{III}-N_{II}-H_{IV}$	103°13′
	$N_{II}-H_{IV}$	1.28	(2) $H_{III}-N_{II}-H_{VI}$	109°59′
	(2) $N_{II}-H_{VI}$	1.03	(2) $H_{IV}-N_{II}-H_{VI}$	105°54′
	mean	1.16	mean	106°33′

crystallographically nonequivalent atoms is: $\Delta\varphi_N = 5$ V, $\Delta\varphi_O = 10$ V, $\Delta\varphi_H = 6$ V.

TABLE 4. Interatomic N–O Distances (in A)

N_I-O_I	2.73	$N_{II}-O_{II}$	2.85
N_I-O_{II}	3.29	$N_{II}-O_{II}$	2.94
(2) N_I-O_{II}	3.01	$N_{II}-O_I$	3.06
(2) N_I-O_{III}	3.12	(2) $N_{II}-O_{III}$	2.53
(2) N_I-O_{III}	3.13	(2) $N_{II}-O_{III}$	2.92
(2) N_I-O_{III}	3.20	(2) $N_{II}-O_I$	3.46

In a comparison of F_t, calculated from the final values of the atomic coordinates, with F_e corrected for extinction according to Blackman, we established a final value of R for all 639 reflections = 36%; the F_e values of the h0*l* reflections shown in Table 2 yield an R = 34%.

From the atomic coordinates shown in Table 1, we calculated the interatomic distances and angles of the SO_4 and NH_4 tetrahedra (Table 3) and some other important distances (Table 4).

Analysis of the Structure

The structure of $(NH_4)_2SO_4$ is constructed of SO_4^{2-} tetrahedra and two types of NH_4^+ tetrahedra. These tetrahedra are irregular, yet they retain symmetry planes which coincide with the planes y = $^1/_4$ and y = $^3/_4$. The S–O distances in the SO_4 tetrahedra vary from 1.34 to 1.61 A, the angles vary from 104°21' to 111°6', which somewhat exceeds the usual scatter of values of distances and angles. However, the mean S–O distance is 1.49 A, and the mean O–S–O angle is 108°; these agree well with the data known in the literature [20].

In the $(NH_4)_I$ tetrahedron the distances and the angles vary within the N–H range from 1.03 to 1.15 A (mean value of 1.08 A) and H–N–H from 94°25' to 119°5' (mean value of 109°39'). In the $(NH_4)_{II}$ tetrahedra the variation is within the range 1.03 to 1.28 A for N–H distances (mean value of 1.16 A)and from 103°13' to 109°59' for H–N–H angles (mean of 106°33'). It must be pointed out that the mean value of the N–H distances in the $(NH_4)_{II}$ tetrahedron is significantly larger than the

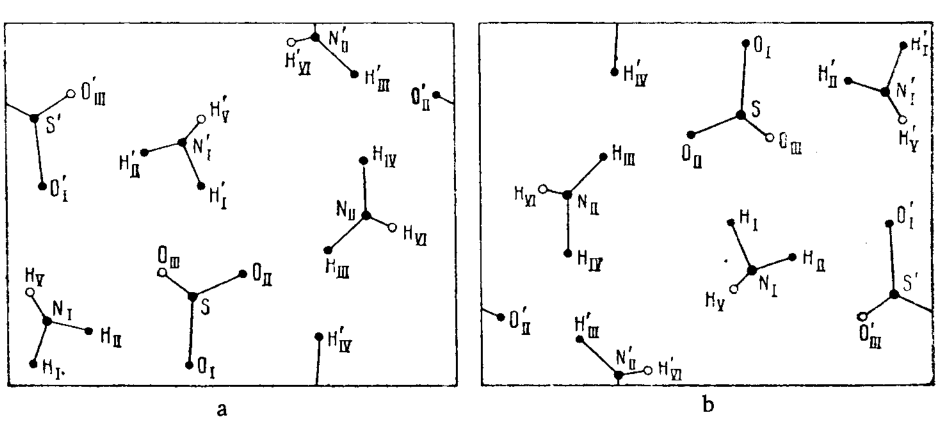

Fig. 6. Sketch of the structure of $(NH_4)_2SO_4$: a) projection on the plane y = $^1/_4$ of atoms which lie between the planes y = 0 and y = $^1/_2$; b) projection on the plane y = $^3/_4$ of atoms which lie between the planes y = $^1/_2$ and y = 1. Black dots represent atoms in the plane of symmetry; white dots represent atoms in general positions.

mean value of these distances in the $(NH_4)_I$ tetrahedron. In addition, the N−H distances and their mean values exceed the values of these distances given in the literature [22]. A sketch of the structure of $(NH_4)_2SO_4$ is presented in Fig. 6.

The $(NH_4)_I$ ion has 10 near neighbors, the distances to which are shown in Table 4; the nearest N_I-O_I distance, 2.73 A, lies in a symmetry plane. The number of nearest neighbors of the $(NH_4)_{II}$ complex is 9, but these oxygen atoms are situated significantly closer to the N atom; there are 6 N−O distances less than 3.00 A, and two of them lie on a symmetry plane, with the other four almost normal to it. In this structure, as in Rochelle salt, the shortest hydrogen bond to $N_{II}-O_{III}$ is almost parallel to the Y axis, which upon transformation of $(NH_4)_2SO_4$ to the ferroelectric state becomes the ferroelectric axis.

Although it is impossible to determine a quantitative criterion, however it must be assumed that the appreciable deformation of the NH_4 tetrahedra is related to the presence and directional nature of hydrogen bonds. This probably explains the fact that in compounds which do not contain hydrogen bonds the deformation of the tetrahedra is much smaller. It must also be pointed out that a reverse relationship has been observed between the N−H and N−O distances.

Attention must be directed to an interesting peculiarity of the hydrogen bonds in this structure; the nearest atoms of hydrogen lie to one side of striaght lines connecting O and N atoms which take part in that bond. The distance of the hydrogen atoms from that N−O straight line series is 0.3-0.5 A. As is known, the "deflectability" of hydrogen bonds has recently been examined in a number of papers and is explained by the rigidity of the angle of the covalent bond to the appropriate atoms [23].

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