Fig. 2. Stereoscopic representation of the thermal ellipsoids for β-isoprene sulfone.

tors for the hydrogen atoms. The hydrogen atom temperature factors, assigned a value of 6·0, were not refined. The final weighted index was 0·041. The maximum value of the final parameter shifts divided by the estimated standard deviations was 0·14 for the non-hydrogen atoms and 0·20 for the hydrogen atoms. Final atomic parameters are shown in Table 1. Bond lengths and angles were calculated using the *BONDLA* program of X-ray 63 (Stewart, 1964) and are shown in Table 2. The observed and final calculated structure factors are shown in Table 3.

Results

Table 2 summarizes the bond lengths and bond angles of β-isoprene sulfone (this paper) and, for comparison, of butadiene sulfone (Sar.ds & Day, 1967). Equivalent dimensions in the two compounds are quite similar. The C(2)–C(3) bond distance of 1·307 Å is significantly shorter than the value of 1·37 Å reported by Jeffrey (1951) but now agrees well with the equivalent value of 1·299 Å observed in butadiene sulfone. Other distances and angles are in agreement with those observed in a variety of sulfones as discussed by Sands & Day. The ellipsoids of atomic thermal vibration are shown in Fig. 2. As expected, the thermal motion of the methyl carbon atom is larger than that of the ring carbon atoms.

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The wurtzite z parameter and linear compressibilities for NH₄F*. By B. MOROSIN, *Sandia Laboratories, Albuquerque, New Mexico* 87115, *U.S.A.*

The z parameter in NH₄F has been determined using 108 Mo $K\alpha$ intensity data to be $0·3781 \pm 0·0007$. The values of the N–F hydrogen bond separations are 2·707 (5) and 2·709 (5) Å. The linear compressibilities along **a** and **c** are 13·6 and $14·6 \times 10^{-13}$ cm².dyne⁻¹, respectively.

Introduction

The phase diagram of ammonium fluoride has received much attention and has been summarized by Nabar, Calvert & Whalley (1969). The structure of NH₄F(II), obtained at 3·64 kbar pressure (Morosin & Schirber, 1965), has yet to be determined. The two initial objectives of the present pressure studies on NH₄F(I) were to determine the compressibilities of the lattice and the pressure change of the wurtzite z parameter prior to the phase transition. An earlier study (Morosin & Schirber, 1969) on the metals Sb and Bi indicated that with proper care and conditions, small differences in structural parameters as a function of pres-

sure could be determined. Unfortunately, this did not prove possible for NH₄F(I). The present study reports the linear compressibilities for NH₄F(I) below this pressure phase transition as well as the redetermination of the structure for the room-temperature one bar phase.

Structure analysis

NH₄F(I) crystallizes with the wurtzite structure in space group $P6_3mc$. In this structure type, the heavy atoms are assigned to special positions on (*b*) sites at $\frac{1}{3},\frac{2}{3},z$ and $\frac{2}{3},\frac{1}{3},\frac{1}{2}$ + z while the hydrogen atoms occupy one such set of sites as well as the sixfold (*c*) sites at $x,\bar{x},z;x,2x,z;2\bar{x},\bar{x},z;\bar{x},x,$ $\frac{1}{2}+z; \bar{x},2\bar{x},\frac{1}{2}+z$ and $2x,x,\frac{1}{2}+z$. In this polar space group, one of the atoms may be assigned $z=0·0$. For the remaining heavy atom, Zachariasen (1927) found $z=0·365$. This result

leads to two very different N–F hydrogen bond separations.

Lattice constants used were $a_0 = 4\cdot4389$ (4) and $c_0 = 7\cdot1635$ (4) Å which were determined previously by the powder method (Morosin & Schirber, 1965). The 108 Mo $K\alpha$ intensity data were measured with a scintillation counter employing pulse-height discrimination using the θ–2θ scan technique.

Structure factors were calculated using F^{-1}, N and H scattering factors from *International Tables for X-ray Crystallography* (1962). The choice of the neutral atom scattering factor for nitrogen was based on the estimates of $+0\cdot28$ and $+0\cdot18$ as charges on the nitrogen and hydrogen atoms, respectively (Pauling, 1960). In our least-squares refinement, the function $= \sum w(F_o - F_c)^2$ was minimized with weights assigned from counting statistics or, for the 10 reflections considered unobserved, set equal to zero whenever $|F_o| > |F_c|$. Initially only the heavy atoms were included in the refinement, and the corresponding difference Fourier synthesis yielded positions for hydrogen atoms consistent with the expected bonding network. Refinement of anisotropic thermal factors for the heavy atoms yielded values within 2σ of the isotropic value; in addition, the correlation between variables, particularly the thermal parameters, was rather high. Therefore, only isotropic thermal parameters are given in Table 1. These parameters yield an R value, where $R = \sum ||F_o| - |F_c||/\sum |F_o|$, equal to 0·046. The observed and calculated structure factors are given in Table 2.

Table 1. *Atomic positional and thermal coordinates for* NH4F

	x	y	z	B
F	$\frac{1}{3}$	$\frac{2}{3}$	0·0	2·53 (10)
N	$\frac{1}{3}$	$\frac{2}{3}$	0·3781 (7)	2·61 (8)
H(1)	$\frac{1}{3}$	$\frac{2}{3}$	0·217 (12)	0·35 (139)
H(2)	0·440 (17)	−0·440	0·421 (7)	4·11 (84)

Table 2. *Observed and calculated structure factors for* NH4F

h	k	l	100Fo	100Fc	h	k	l	100Fo	100Fc	h	k	l	100Fo	100Fc
1	0	0	1697	-1617	1	0	3	1266	-1361	0	0	6	477	488
2	0	0	815	-781	2	0	3	934	891	1	0	6	226	-226
3	0	0	893	887	3	0	3	040	-024	2	0	6	200	-188
4	0	0	250	-247	4	0	3	309	-304	3	0	6	252	252
5	0	0	131	-134	5	0	3	164	174	4	0	6	070	-079
1	1	0	2074	2027	1	2	3	677	633	1	1	6	398	393
1	2	0	622	-584	1	3	3	395	-379	1	2	6	142	-142
2	2	0	713	677	2	3	3	253	251	2	2	6	198	204
1	3	0	303	-298	1	4	3	031	000	1	3	6	096	-098
2	3	0	202	-199	2	4	3	139	-148	2	3	6	059	-066
3	3	0	224	239	1	5	3	117	125	1	4	6	111	120
1	4	0	334	344										
2	4	0	110	-113	0	0	4	376	381	1	0	7	230	201
1	5	0	084	-094	1	0	4	164	-165	2	0	7	168	-156
					2	0	4	140	-122	3	0	7 L	030	004
1	0	1	991	-1013	3	0	4	122	128	4	0	7	069	072
2	0	1	651	624	4	0	4	030	-029	1	2	7	125	-123
3	0	1	079	-036	5	0	4 L	033	-012	1	3	7	083	087
4	0	1	176	-174	1	1	4	258	258	2	3	7	055	-062
5	0	1	086	091	1	2	4	072	-079					
1	2	1	456	433	2	2	4	074	090	0	0	8	389	372
1	3	1	226	-224	1	3	4	045	-042	1	0	8	184	-174
2	3	1	131	136	2	3	4 L	031	-022	2	0	8	155	-146
1	4	1 L	029	000	3	3	4 L	034	021	3	0	8	214	215
2	4	1	067	-075	1	4	4 L	032	036	1	1	8	317	308
1	5	1	057	·063	2	4	4 L	034	-010	1	2	8	119	-120
										2	2	8	174	181
0	0	2	2029	2199	1	0	5	829	806	1	3	8	080	-086
1	0	2	936	-864	2	0	5	601	-584					
2	0	2	457	-440	3	0	5 L	027	-010	1	0	9	070	-073
3	0	2	553	538	4	0	5	226	237	2	0	9	062	060
4	0	2	165	-157	5	0	5	127	-141	3	0	9 L	034	001
5	0	2	089	-087	1	2	5	442	-442	1	2	9	046	051
1	1	2	1071	1133	1	3	5	283	289					
1	2	2	385	-350	2	3	5	188	-199	0	0	10	143	150
2	2	2	440	421	1	4	5 L	033	000	1	0	10	066	-071
1	3	2	186	-185						2	0	10	058	-060
2	3	2	152	-128						1	1	10	122	127
3	3	2	150	156										
1	4	2	219	221										
2	4	2	073	-074										
1	5	2	056	-061										

If the tetrahedron, formed by the four nearest-neighbor fluoride ions about the ammonium ion, is assumed to be oriented with the apex located along the c axis, the N–F interatomic separation toward the apex is 2·709 (5) Å while those toward the base are 2·707 (5) Å. The F–N–F angles formed by the base fluoride ions are 110·1 (2)° while those involving the apex fluoride ion are 108·8 (2)°. Because of the large standard deviation for the parameters involving the hydrogen atoms, the two N–H separations, 1·16 and 0·88 Å, cannot be considered significantly different from the expected 1·03 Å value and the isotropic temperature factors must be considered identical. Hence, a neutron diffraction study will be necessary to corroborate the suggestion of Drain (1955) that the probable thermal motion of the ammonium ion involves rotation about the threefold axis.

Pressure results

Lattice constants as a function of pressure were determined using a beryllium pressure cell described elsewhere (Morosin & Schirber, 1969). 2θ values for eight reflections (in the range 105–150° with Cu $K\alpha$ radiation) were used in the least-squares procedure. These results are summarized on Fig. 1. The linear compressibilities along **a** and **c** are 13·6 (5) and 14·6 (5) $\times 10^{-13}$ cm². dyne^{-1}, respectively. These compressibilities yield only a very slight change in the c/a ratio (1·6138 to 1·6129) at the 3·64 kbar phase transition and hence, do not suggest the mechanism for formation of NH4F(II).

A detailed pressure study of the 'z' parameter was not carried out because the standard deviation of this 1 bar study is about one order of magnitude larger that that obtained in our previous pressure study on Sb and Bi. In
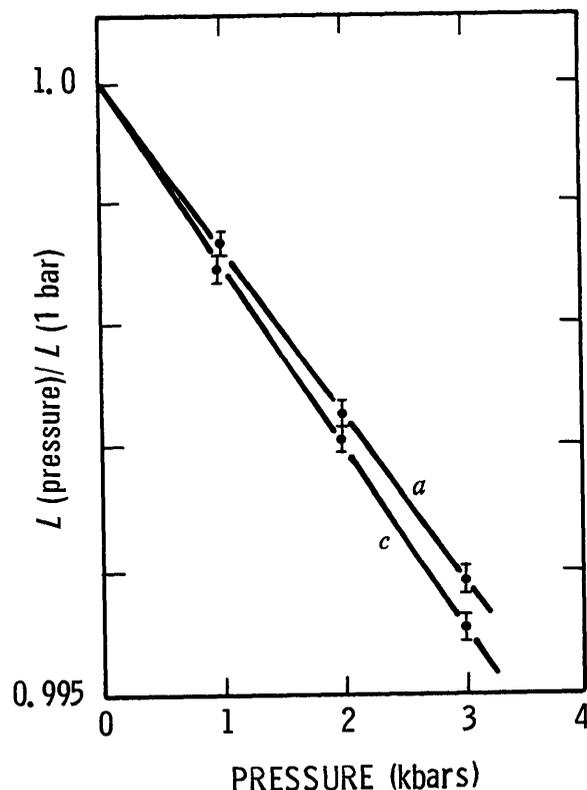

Fig. 1. Reduced lattice constants *versus* pressure.

addition, the compressibilities along **a** and **c** are almost identical, suggesting that the minimum in the crystalline energy would require the two N–F separations to remain nearly identical in length.

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International Union of Crystallography

Commission on Crystallographic Apparatus

Phase II of the I. U. Cr. Single Crystal Intensity Measurement Project

An International Project which will be phase II of the Single Crystal Intensity Measurement Project, SCIMP (Abrahams, Hamilton & Mathieson, 1970), is proposed by the Commission on Crystallographic Apparatus of the International Union of Crystallography. The plan of the phase II project is for each participant (individual or group) to derive for a specific material, α-glycine, a set of experimental structure factors, F_o, as independent of the individual crystal as possible. To this end, corrections for absorption and extinction will be obligatory. The aim of the project is to determine the measure of accord achieved by the participants over a range of crystals, diffractometers and techniques and also to obtain some guide as to the efficacy of experimental procedures for the diagnosis and correction of extinction effects.

The reasons for initiating phase II of SCIMP derive from the results of phase I, the report on which clearly indicated that, for the material used, D(+)-tartaric acid, the particular characteristics of the individual crystal constituted the major source of error in the derivation of accurate F_o values. The functional trend of the differences between F values for different crystals has identified extinction as the main error factor. There is therefore an obvious need to extend the earlier intensity measurement project to a second stage in which the effects of differences between individual crystals are diagnosed and minimized. To reduce measurements from different crystals to a more or less common base, it is necessary that corrections be applied, not only for simple absorption but also, and probably more importantly, for extinction. Correction procedures for simple absorption are relatively straightforward but there is no single preferred procedure for the estimation of extinction effects. Since theoretical F_c values are dependent on the particular model adopted, reference to such values as a guide or measure of experimental accuracy is questionable. It seems therefore more appropriate to test, as far as possible, *experimental procedures which are intended to diagnose and correct for extinction.*

There are a number of feasible procedures for the estimation of extinction which are essentially experimental. These involve either measurements on the one specimen or measurements on two (or more) specimens – for example:

(*a*) with a single specimen,
   (i) measurements with a polarization analyser, *e.g.* Chandrasekhar *et al.* (1969);
   (ii) measurements made at two or more wavelengths, *e.g.* DeMarco & Weiss (1962);
   (iii) measurements of integrated intensity with varying path lengths as achieved, for instance, by rotation about the scattering vector, *e.g.* Willis (1962).

(*b*) with more than one specimen,
   (i) comparison with measurements on powdered specimens of the same material, *e.g.* Stewart & Jensen (1969);
   (ii) measurements on single crystals of different size, or extinction condition, and appropriate extrapolation, Cochran (1953).

Any other suitable procedure, not specified above, but of an experimental nature may be used.

The Commission welcomes the cooperation of crystallographers in this project. Its successful operation will obviously depend critically on their willingness to participate. It is recognized that the proposed project is not a simple straightforward one but, just as phase I focused attention on the potential gross effect of specimen variation, so Phase II could be most valuable and instructive in highlighting the magnitude and significance of intensity-dependent factors in experimental measurements and should assist in assessing the scope of operational procedures for estimating extinction.

Any individual crystallographer or group wishing to have further details should contact the Chairman – Dr A. McL. Mathieson, Division of Chemical Physics, C.S.I.R.O., P.O. Box 160, Clayton, Victoria 3168, Australia.

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