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Phase Relations of NH_4ClO_4 and NH_4BF_4 to High Pressures

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The high pressure phase diagrams of NH_4ClO_4 and NH_4BF_4 were studied by means of differential thermal analysis and volumetric techniques. The high temperature portions of these diagrams are intermediate between those of the corresponding potassium and rubidium salts, but at low temperatures the onset of hydrogen bonding causes the appearance of phases which are unique to the ammonium compounds.

Introduction

The high pressure polymorphism of the univalent perchlorates was first studied by Bridgman (*1*) to 50 kbar and ~100°C. There have been recent studies of the complete phase diagrams to ~40 kbar of $NaBF_4$, $NaClO_4$ (*2*), $KClO_4$, KBF_4 (*3*), $RbClO_4$, $RbBF_4$ (*4*), $CsClO_4$ and $CsBF_4$ (*5*).

NH_4ClO_4 II and NH_4BF_4 III under ambient conditions have the barite structure and are, therefore, isostructural with the ambient modifications of the corresponding potassium, thallous, rubidium and cesium salts (*6*), as well as with $NaClO_4$ III and $NaBF_4$ IV (*2*). These phases transform to cubic modifications (*6*) with the space group *Fm*3*m* (*2*) at elevated temperatures. The disorder in the structure is not caused by free rotation of the anions, but is of a type which maximizes the cation-oxygen (or cation-fluorine) distances. This transition occurs at 240°C for NH_4ClO_4 (*7*) and at 199°C for NH_4BF_4 (*8*). For KBF_4 (*3*) and $RbBF_4$ (*4*), this phase transforms at still higher temperature and pressure to another modification which was suggested (*4*), on the basis of entropy considerations, also to be cubic, space group *Fm*3*m*, and perhaps possessing the anti-NH_4Cl structure (*9*, *10*). In the case of $CsBF_4$, phase transitions to two other phases, $CsBF_4$ V and $CsBF_4$ VI, occur with probably free rotation of the anion tetrahedra in the $CsBF_4$ V modification (*5*). No corresponding high temperature transitions could be found for the perchlorates of potassium, rubidium, and cesium due to thermal instability of the compounds in the range where such modifications might be expected.

Stammler *et al.* (*11*) reported a phase transition near −190°C for both NH_4BF_4 and NH_4ClO_4 on the basis of changes in unindexed X-ray powder patterns. The heat capacity data for NH_4ClO_4 (*12*) and NH_4BF_4 (*13*) do not support the above results, however. Caron *et al.* (*14*) reported a subtle structural change within the orthorhombic system for NH_4BF_4 at some temperature above −132°C, which correlates with a rotational peak in the heat capacity curve of NH_4BF_4 (*13*). Van Rensburg (*15*) found a transition near −190°C for NH_4ClO_4 and two transitions near −190°C and −95°C for NH_4BF_4 by means of infrared spectroscopy. The transition at −95°C was confirmed by means of single-crystal X-ray analysis.

Experimental

NH_4ClO_4 with a purity of 99+% was obtained from B.D.H. Technical grade NH_4BF_4, also obtained from B.D.H., was purified by recrystallization from an aqueous solution and thorough drying before use.

Pressures up to 40 kbar were generated in a piston-cylinder apparatus (*16*, *17*). Phase changes were studied by means of differential thermal analysis (DTA) (*16*, *18*) using Chromel–Alumel thermocouples. Heating/cooling rates were in the order of 0.3–1.4°C/sec. The detailed experimental procedure has been described elsewhere (*4*, *5*). Phase boundaries were taken to be the mean of the heating and cooling temperatures and were based on several consistent runs. The observed boundaries are believed to be within 2°C and 0.5 kbar. High pressure phase changes were studied by means of volume displacement (*5*, *19*) and piston-rotation techniques (*17*), also previously described (*4*).

Results

Ammonium Perchlorate

The phase diagram of NH_4ClO_4 is shown in Fig. 1. The II/I transition yielded strong and clear signals at atmospheric pressure (Fig. 2(vi)). The dependence of the II/I transition temperature at atmospheric pressure on the heating/cooling rate is shown in Fig. 3. The transition temperature was found to be 238.1 ± 1.0°C, being the mean of 18 determinations, as compared to the literature value of 240°C (*8*). The transition was followed to ~4 kbar and 300°C. NH_4ClO_4 exploded violently in the range 330–350°C at 2–3.6 kbar, although at atmospheric pressure it is known to explode only at ~440°C (*20*, *21*). The transition signals, though still clear, became smaller and broader at higher pressures. This is due to the large volume change upon transition, which causes a local pressure increase at

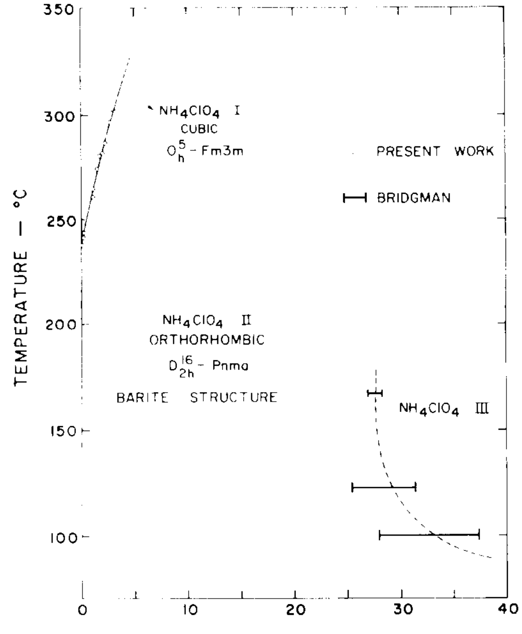

FIG. 1. Phase diagram of NH_4ClO_4 to 40 kbar.

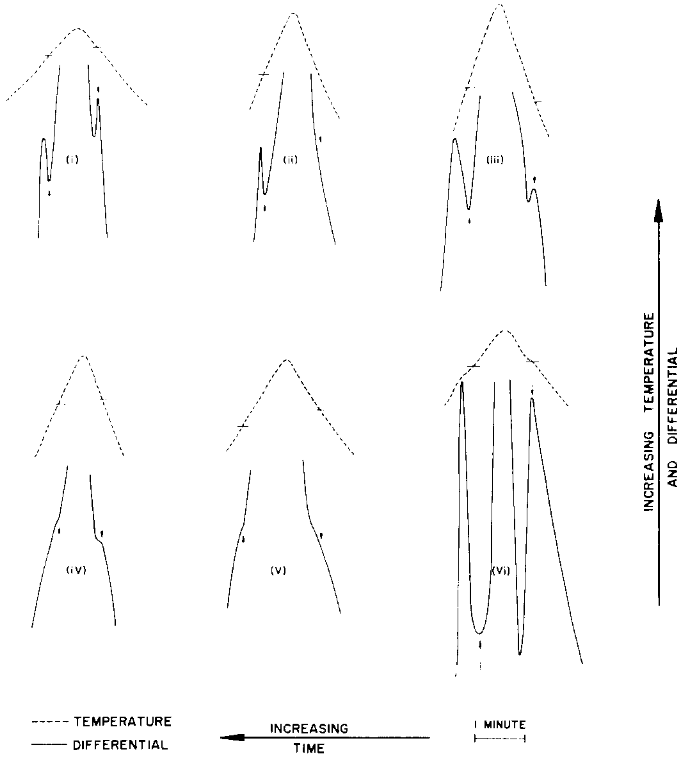

FIG. 2. Typical DTA signals obtained: (i) NH_4BF_4 III/II at 0 kbar, 192.2°C heating, 186.7°C cooling. (ii) NH_4BF_4 II/I at 14.3 kbar, cooling at 581.5°C. (iii) NH_4BF_4 I/liquid at 5.9 kbar, 597.2°C heating, 607.1°C cooling. (iv) NH_4BF_4 VI/II at 11.25 kbar, 471.0°C heating, 467.8°C cooling. (v) NH_4BF_4 VI/I at 21.1 kbar, 625.3°C heating, 617.3°C cooling. (vi) NH_4ClO_4 II/I at 0 kbar, 241.2°C heating, 238.4°C cooling.

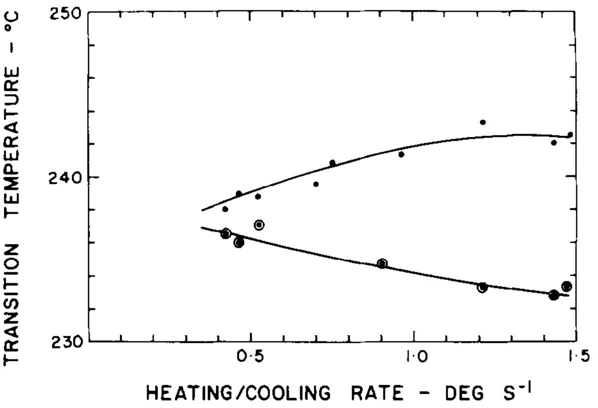

FIG. 3. Dependence on the rate of heating and cooling of the NH_4ClO_4 II/I transition temperature at atmospheric pressure; ●—heating, ⊙—cooling.

the sample. No other transitions could be detected down to −150°C at atmospheric pressure. The phase relations of NH_4ClO_4 are summarized in Table I.

Ammonium Tetrafluoroborate

The phase diagram of NH_4BF_4 is shown in Fig. 4. The NH_4BF_4 III/II transition yielded sharp and clear DTA signals at atmospheric pressure (Fig. 2(i)). The signals became broader at higher pressures, as in the case of NH_4ClO_4, but remained clear. The NH_4BF_4 III/II transition was less dependent on the heating/cooling rate than the corresponding NH_4ClO_4 II/I transition (compare Figs. 3 and 5). The transition point at atmospheric pressure was 188.8 ± 0.5°C, being the mean of 22 determinations. This value is lower than the literature values of 199°C (*8*) and 236°C (*11*). The high literature values may be due to sublimation or decomposition known (*22, 23*) to occur when uncontained NH_4BF_4 is heated above ~110°C.

The III/II transition line rises steeply with pressure to a triple point NH_4BF_4 III/II/VI at 8.3 kbar, 379°C, but it was possible to obtain several points on the metastable extension of the III/II phase boundary into the stability field of NH_4BF_4 VI. The VI/II phase transition yielded broad DTA signals (Fig. 2 (iv)) similar to those due to the III/II transition, and was terminated at a triple point NH_4BF_4 VI/II/I at 18.3 kbar, 587°C with the appearance of a further new phase NH_4BF_4 I. The VI/I transition yielded broad ill-defined DTA signals (Fig. 2(v)) which were difficult to measure accurately. The II/I transition, on the other hand, yielded only a broad inflection upon heating, but a clear and sharp signal upon cooling (Fig. 2(ii)). The II/I transition line is based only upon cooling points, and extrapolates to ~460°C at atmospheric pressure. NH_4BF_4 apparently decomposes at atmospheric pressure before this temperature is reached. For the same reason, no melting signals could be obtained at atmospheric pressure, but the melting curve of NH_4BF_4 I at elevated pressures yielded sharp and clear DTA signals (Fig. 2(iii)). The melting curve extrapolates to ~510°C at atmospheric pressure.

The NH_4BF_4 III/VI phase transition, inferred above from the observation of a possible triple point III/II/VI, was confirmed by means of volume discontinuity. A typical plot of piston displacement

TABLE I

PHASE RELATIONS OF NH_4ClO_4 AND NH_4BF_4

Transition line	Fit	Standard deviation
NH_4ClO_4 I/II	$t(°C) = 21.6P + 238.1$	2.3 deg
NH_4BF_4 III/II	$t(°C) = 189 + 24.7P - 0.221P^2$	0.37 kbar
NH_4BF_4 II/I	$t(°C) = 460 + 18.5P - 1.02P^2 + 0.02P^3$	0.88 kbar
NH_4BF_4 I/liquid	$P/3.44 = (T/510)^{9.46} - 1$	2.7 deg
NH_4BF_4 VI/II	$t(°C) = 379 + 30.4(P - 8.3) - 0.963(P - 8.3)^2$	0.4 kbar
NH_4BF_4 VI/I	$t(°C) = 587 + 9.55(P - 18.3) - 0.056(P - 18.3)^2$	4.7 deg
Triple point	*Pressure (kbar)*[a]	*Temperature (°C)*[a]
NH_4BF_4 VI/III/II	8.3	379
NH_4BF_4 I/VI/II	18.3	587
NH_4BF_4 VI/V/III	~14	~56
NH_4BF_4 V/IV/III	~3	~120

[a] The accuracy of the triple points is best judged from Fig. 4.

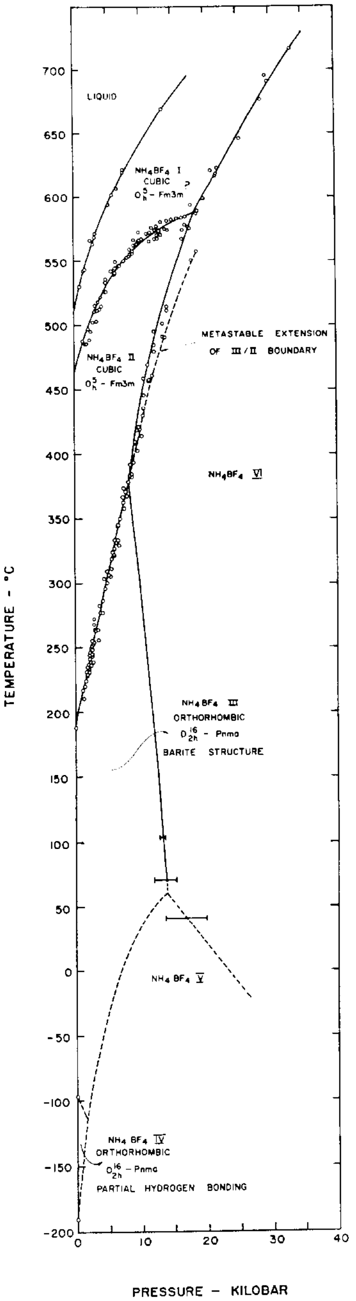

FIG. 4. Phase diagram of NH_4BF_4 to 40 kbar.

versus load is shown in Fig. 6. The volume change was found to be

$$\Delta V_{VI/III} = 0.9\ \text{cm}^3/\text{mole}$$

at 104° and 70.8°C. A run at 41.6°C, however, yielded a volume change of only 0.5 cm^3/mole, and a transition pressure considerably higher than expected. This tentatively implies the possibility of a further triple point near 14 kbar, 56°C, which will be further discussed below. No clear indications of a transition could be observed at 23°C. The transition pressures obtained by piston rotation are listed in Table II.

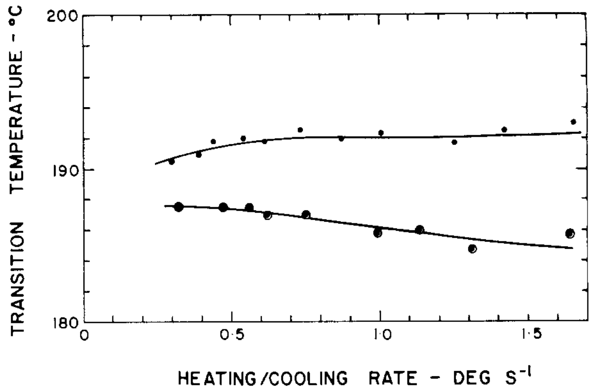

FIG. 5. Dependence on the rate of heating and cooling of the NH_4BF_4 II/III transition temperature at atmospheric pressure; ●—heating, ⊙—cooling.

The phase relations of NH_4BF_4 are summarized in Table I.

Discussion

Van Rensburg (*15*) recently showed that NH_4BF_4 IV, the phase stable between −95°C and −190°C at atmospheric pressure, is orthorhombic with the same space group as NH_4BF_4 III. The structure of NH_4BF_4 IV differs from that of NH_4BF_4 III in that partial hydrogen bonds H—F exist, thereby distorting the barite structure slightly. Geometrical considerations prevent complete hydrogen bonding of all adjacent H—F pairs. Furthermore, the III/IV transition takes place with an *increase* in volume, i.e., NH_4BF_4 IV is ~1% denser than NH_4BF_4 III at the transition point. It is to be expected that NH_4BF_4 V below −190°C will exhibit complete hydrogen bonding of all adjacent H—F pairs, and that NH_4BF_4 V will be denser than NH_4BF_4 V at −190°C. These results are in agreement with the present observation of a possible triple point NH_4BF_4 VI/V/III near 14 kbar, 56°C. The difference of 0.4 cm^3/mole between $\Delta V_{VI/III}$ and $\Delta V_{VI/V}$ implies that

$$\Delta V_{V/III} = 0.4\ \text{cm}^3/\text{mole}$$

near the NH_4BF_4 VI/V/III triple point, and the dotted phase boundaries drawn in Fig. 4 become plausible. In particular, it is only possible to obtain a consistent phase diagram if the NH_4BF_4 V/IV/III triple point is located below ~5 kbar. This implies

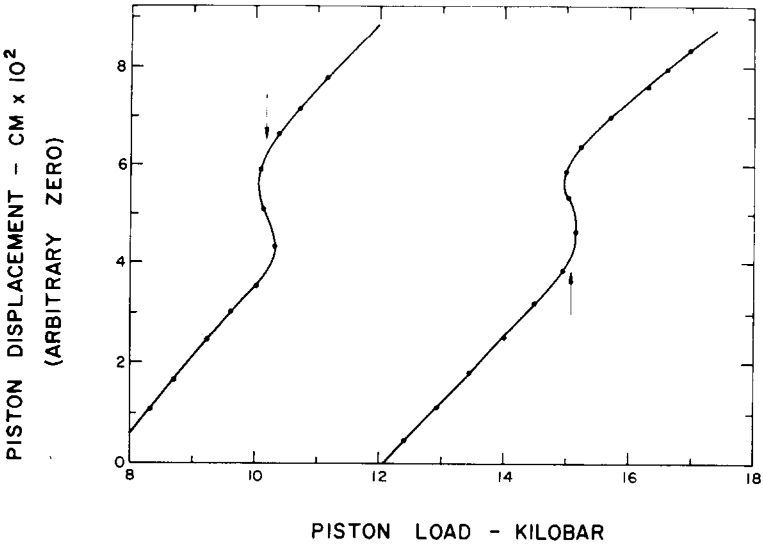

FIG. 6. Curves of piston displacement versus piston load for NH_4BF_4 at 104°C, showing the III/IV transition. The S-shape of the curves may be due to nucleation phenomena.

that NH_4BF_4 IV is more or less merely an intervening phase which is stabilized mainly by the interplay between thermal disorder, on the one hand, and the geometrical distortion caused by the tendency towards hydrogen bonding, on the other. This tendency can be expected to be somewhat weaker in NH_4ClO_4, and it is therefore not surprising that no phase similar to NH_4BF_4 IV is found in the phase diagram of NH_4ClO_4. Instead, the transition from the barite-type structure to the, presumably, ordered hydrogen-bonded structure occurs directly as for NH_4BF_4 above ~5 kbar.

The NH_4BF_4 V/VI transition is extremely sluggish even at 41.6°C, and becomes unobservable, as was the III/V transition, at room temperature. The III/VI transition, however, runs slowly, but with only a small region of indifference, at ~100°C. Nevertheless, the fact that the metastable extension of the III/II phase boundary could be followed by means of rapid DTA methods to considerably beyond the NH_4BF_4 VI/III/II triple point indicates that even at this temperature the III/VI transition is still a slow phase change.

TABLE II

TRANSITION PRESSURES AFTER PISTON ROTATION

Transition line	Upstroke pressure (kbar)	Downstroke pressure (kbar)	Temperature (°C)
NH_4BF_4 III/VI	13.65	13.17	104.0
	15.49	12.09	70.8
NH_4BF_4 V/VI	20.04	13.77	41.6

The slope of the NH_4ClO_4 II/I transition line is 21.6 deg/kbar, which, together with the observed transition entropy, viz., 18.8 J/mole-deg (*24*), yields

$$\Delta V_{\mathrm{II/I}} = 4.1\ \mathrm{cm^3/mole}$$

for the volume change upon transition. Due to the onset of sublimation even below the transition point, the entropy of the NH_4BF_4 III/II transition is not known. However, the entropy of the corresponding transitions from barite-type to cubic *Fm*3*m* is close to R ln 8 for NH_4ClO_4 as well as the perchlorates and tetrafluoroborates of Cs, Rb, Tl and K, and it may be assumed that this is the case also for the NH_4BF_4 III/II transition. The initial slope of the transition line is 24.7 deg/kbar, yielding, therefore,

$$(\Delta V_{\mathrm{III/II}})_{P=0} = 4.3\ \mathrm{cm^3/mole},$$

while at the NH_4BF_4 VI/III/II triple point, with a slope of 21.1 deg/kbar and assuming that $\Delta S_{\mathrm{III/II}}$ still nearly equals R ln 8,

$$(\Delta V_{\mathrm{III/II}})_{P=8.3\mathrm{kbar}} = 3.7\ \mathrm{cm^3/mole}.$$

The mean slope of the III/VI boundary is −56 deg/kbar, and $\Delta V_{\mathrm{III/VI}} = -0.9\ \mathrm{cm^3/mole}$. Therefore,

$$\Delta S_{\mathrm{III/VI}} \simeq 1.7\ \mathrm{J/mole\text{-}deg}$$

and, if we assume approximate constancy of the entropy changes along the transition lines,

$$\Delta S_{\mathrm{VI/II}} \simeq 15.6\ \mathrm{J/mole\text{-}deg}$$

and

$$(\Delta V_{\mathrm{VI/II}})_{P=8.3\,\mathrm{kbar}} \simeq 4.6\ \mathrm{cm}^3/\mathrm{mole}$$

from the additive relations at the triple point. The independent calculation from the initial slope of the VI/II transition line, viz., 30.4 deg/kbar, yields

$$(\Delta V_{\mathrm{VI/II}})_{P=8.3\,\mathrm{kbar}} \simeq 4.8\ \mathrm{cm}^3/\mathrm{mole}$$

in excellent agreement.

An extension of these arguments to involve NH_4BF_4 I, while possible, is of little value in view of the experimental uncertainty in the slope of the VI/II phase boundary near the VI/II/I triple point. It is clear from Fig. 4, for instance, that this triple point could equally well be located as low as 17 kbar. This would markedly affect the curvature and final slope of the VI/II transition line.

The curvature of the melting curve of NH_4BF_4 I suggests that a triple point NH_4BF_4 VI/I/liquid may occur near ~50 kbar, above which pressure NH_4BF_4 VI will melt directly.

A comparison of the phase diagram of NH_4BF_4 with that of, for instance, KBF_4 (*3*), $RbBF_4$ (*4*) or $CsBF_4$ (*5*), reveals close similarities. Specifically, it would appear probable that NH_4BF_4 I is a phase similar to KBF_4 III, $RbBF_4$ IV and $CsBF_4$ I, while NH_4BF_4 VI is similar to $RbBF_4$ III and $CsBF_4$ IV. The low temperature phases NH_4BF_4 IV and V cannot, on the basis of the structural information (*15*), be expected to have counterparts in the phase diagrams of simpler tetrafluoroborates or perchlorates.

It is tempting to assume that the anomalous curvature of Bridgman's (*1*) NH_4ClO_4 II/III transition line near 100°C is due to a triple point involving the phase found at atmospheric pressure below −190°C. This is possible, but it should be kept in mind that no sudden decrease in the transition volume change was found in this case. Nevertheless, it would be surprising if NH_4ClO_4 III prove to have a structure different from NH_4BF_4 VI.

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