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Melting Curve and High-Pressure Polymorphism of NH_4HF_2

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The melting curve of NH_4HF_2 I rises from 125.2°C at atmospheric pressure to a triple point II/I/liquid at 9.3 kbar, 220°C. The I/II phase boundary is terminated at a triple point III/I/II at ~45 kbar, 295°C. The melting curve of the new phase NH_4HF_2 II passes through a broad maximum at ~39 kbar, 306°C, and is terminated at a triple point III/II/liquid at 46.3 kbar, 301°C. The melting curve of NH_4HF_2 III rises with pressure. The NH_4HF_2 III may be a dense hydrogen-bonded phase. Liquid NH_4HF_2 appears to be anomalous in several respects, and has a high compressibility relative to the solid phases.

Introduction

An extended study of the phase diagrams of the univalent perchlorates and tetrafluoroborates (*1–5*) has shown that the polymorphism of the alkali metal salts follow a regular pattern throughout the series, with, as is usual for ionic salts, large cationic radius simulating high pressures. Above ~60°C the ammonium salts behave in the same way as the alkali metal salts, but below this temperature, and especially below ~−190°C, hydrogen-bonded phases of NH_4ClO_4 and NH_4BF_4 exists (*5, 6*).

The lighter alkali metal bifluorides are monoclinic or rhombohedral at ambient conditions, with distorted NaCl-like structures. The KHF_2 and $RbHF_2$ are tetragonal, with a distorted CsCl-like structure, at ambient conditions, but transform to cubic NaCl-like phases at elevated temperatures and low pressures, and to cubic CsCl-like phases at elevated temperatures and pressures. The $CsHF_2$ is also tetragonal, but at atmospheric pressure transforms first to a cubic CsCl-like phase, and then to a phase which is probably cubic NaCl-like (*7–9*). The NH_4HF_2 at ambient conditions has a structure which, although CsCl-like, differs considerably from the other structures in this group. It is orthorhombic, space group D_{2h}^7-*Pman*, and the structure is completely determined by hydrogen bonds (*10*). There are two crystallographically independent examples of each type, viz., N–H—F and F–H–F. Infrared studies show that the ammonium ion is locked in the lattice by hydrogen bonding (*11*), with the H–H—F bonds collinear (*10*).

It is to be expected that the hydrogen bonding would become sufficiently weak at higher temperatures, with resulting thermal motion, to allow the substance to transform to a more ionic phase. The NH_4HF_2 melts at 124.6 ± 0.3°C (*12*) without a change in structure up to that point. However, most order–disorder transition lines have relatively small volume changes and large entropy changes, and it is therefore to be expected that a possible order–disorder transition line would have a relatively small slope dT/dP in the P–T plane. Such a line may thus branch off from the melting curve at higher pressures.

Experimental

The B.D.H. technical-grade NH_4HF_2 was purified by repeated fractional recrystallization from aqueous solution, powdered, and stored in a desiccator over P_2O_5 until use.

Pressures up to 50 kbar were generated in a piston-cylinder device (*13*). The arrangement proposed by Haygarth and Kennedy (*14*) was used for pressures above 40 kbar. High-temperature phase changes were studied by means of DTA, using Chromel–Alumel thermocouples. Heating/cooling rates ranged from 0.4 to 0.7°C/sec. The detailed experimental procedure has been described before

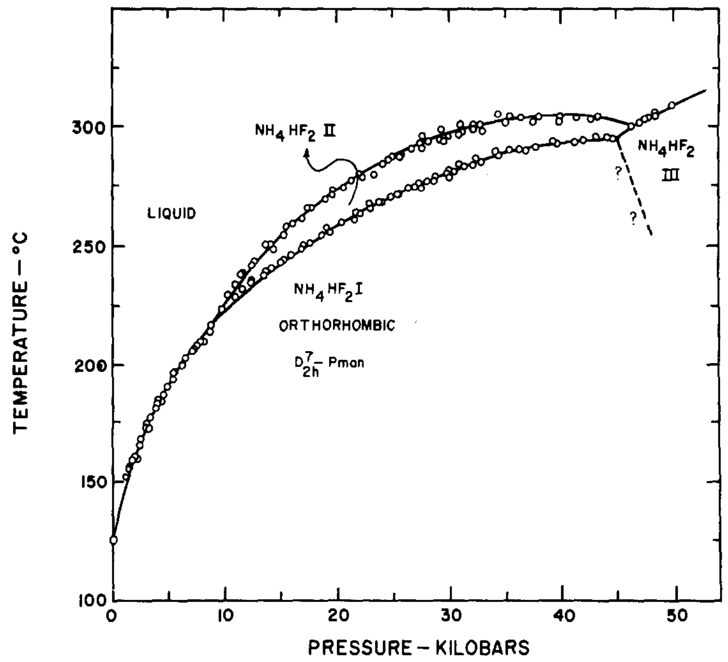

FIG. 1. Phase diagram of NH_4HF_2 to 50 kbar. Dashed lines denote suggested phase boundaries.

(*3*). The final pressures are believed accurate to ±0.5 kbar. The samples were contained in silver capsules. No reaction with the capsule material was observed with dry samples.

Results

The phase diagram of NH_4HF_2 is shown in Fig. 1. The melting temperature at atmospheric pressure was found to be 125.2°C in excellent agreement with the literature value (*12*) of 124.6°C. Melting and freezing of NH_4HF_2 I yielded broadish DTA signals [Fig. 2(i)] with freezing ~1°C below melting at atmospheric pressure, up to 10°C *above* melting while increasing pressure and within ~2°C of melting while decreasing pressure. This apparently anomalous freezing behavior can be ascribed to local higher pressures generated by the very large (see below) volume change upon melting. The melting curve of NH_4HF_2 I rises with pressure with an initial slope of

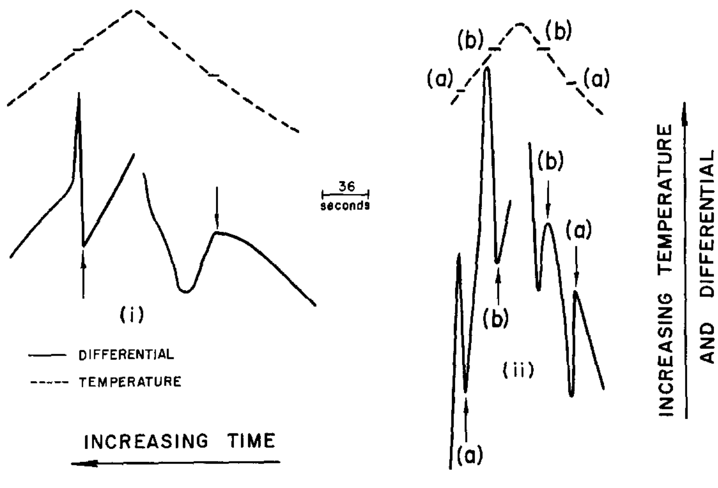

FIG. 2. Typical DTA signals obtained. (i) NH_4HF_2 I/liquid—155.5°C melting at 1.9 kbar, 168.3°C freezing at 2.3 kbar; (ii) (a) NH_4HF_2 I/II transition at 29.3 kbar, 278°C heating, 276°C cooling; (b) NH_4HF_2 II/liquid at 29.3 kbar, 294.0°C.

24°C/kbar, but considerable curvature, to a triple point NH_4HF_2 II/I/liquid at 9.3 kbar, 220°C with the appearance of a new phase NH_4HF_2 II. The slope of the melting curve of NH_4HF_2 I at the triple point is only 5.3°C/kbar. The DTA signals corresponding to the I/II transition and the melting and freezing of NH_4HF_2 II were very sharp [Fig. 2(ii)]. No difference between the melting and freezing temperatures of NH_4HF_2 II could be observed. The thermal hysteresis of the I/II transition was ~2°C for a heating/cooling rate of 0.7°C/sec. The I/II transition line rises with pressure with an initial slope of 4.1°C/kbar and moderate curvature to 44.6 kbar, 295°C, where the signals suddenly disappeared. This behavior was reversible when pressure was released. The slope of the line at this point is 0.1°C/kbar. The melting curve of NH_4HF_2 II rises with pressure with an initial slope of 5.8°C/kbar and considerable curvature, passes through a broad maximum at ~39 kbar, 306°C, and then falls with pressure to a triple point NH_4HF_2 III/II/liquid at 46.3 kbar, 301°C. The DTA signals due to the melting of NH_4HF_2 III were similar to those due to the melting of NH_4HF_2 II. The melting curve of NH_4HF_2 III was followed to 50 kbar, 310°C. No signals corresponding to the suggested III/II or I/III transition lines were observed. The NH_4HF_2 III/II transition line should connect the III/II/liquid triple point with the III/I/II triple point near ~45 kbar, 295°C. The large change of slope of the melting curve at the III/II/liquid triple point demands a large volume change for the I/III transition, and it is not surprising that such a transition line, with necessarily a steep slope, could not be observed by means of DTA methods. At 25°C, the I/III transition pressure must be higher than 40 kbar, as shown by a volumetric study.

The phase relations of NH_4HF_2 are summarized in Table I.

Discussion

The heat of fusion of NH_4HF_2 I at atmospheric pressure is 15.8 ± 0.7 kJ/mole (*15*). The initial slope of the melting curve of NH_4HF_2 I is 24°C/kbar. Using the Clapeyron–Clausius equation, we therefore find

$$(\Delta V_{\mathrm{I/liq}})_{P=0} = 9.5\ \mathrm{cm^3/mole}$$

for the initial volume change upon fusion. This is an increase in volume of ~25%, and suggests that the structure of liquid NH_4HF_2 may be very different from that of solid NH_4HF_2 I. The high curvature of the melting curve of NH_4HF_2 I and the maximum in the melting curve of NH_4HF_2 II are further anomalies which may suggest that liquid NH_4HF_2 might be ionic with no major hydrogen bonding. It is certain that the compressibility of the liquid is anomalously high in comparison with that of the solid, and this would require a rather open "structure" of liquid NH_4HF_2.

The transition from NH_4HF_2 I to II can be expected to involve an increase in disorder due either to one or both of the two types of crystallographically nonidentical groups F–H–F and N–H—F becoming indistinguishable, or to a rupture

TABLE I

PHASE RELATIONS OF NH_4HF_2

Boundary	Fit	Standard deviation
NH_4HF_2 I/liq	$P/2.045 = [T(°\mathrm{K})/398.3]^{8.101} - 1$	1.6°C
NH_4HF_2 I/II	$t(°\mathrm{C}) = 220.3 + 4.14(P - 9.3) - 0.0575(P - 9.3)^2$	1.3°C
NH_4HF_2 II/liq	$t(°\mathrm{C}) = 220.3 + 5.78(P - 9.3) - 0.0974(P - 9.3)^2$	2.9°C
NH_4HF_2 III/II	$t(°\mathrm{C}) \simeq 295 + 5(P - 45)$	—
NH_4HF_2 III/liq	$t(°\mathrm{C}) \simeq 301 + 2.4(P - 46.3)$	0.5°C

Triple point	Pressure[a]	Temperature[a]
NH_4HF_2 II/I/liq	9.3 kbar	220.3°C
NH_4HF_2 III/I/II	~45 kbar	295°C
NH_4HF_2 III/II/liq	46.3 kbar	301°C

[a] The accuracies of the triple points are best judged from Fig. 1.

of the N–H—F bonds resulting in relatively free rotational motion of the ammonium ions, or to a combination of these effects. It is not possible to make a detailed estimate of the structure of NH_4HF_2 II at this stage, but the sharpness and small thermal hysteresis of the I/II transition suggests that the change involved is a small one.

The maximum in the melting curve of NH_4HF_2 II is of considerable interest. Melting curve maxima have been semiquantitatively explained (*16*) on the basis of Klement's model (*17*), which assumes the liquid to consist of two (or more) species, with a continuous transition to a denser species taking place at higher pressures. The less dense species was shown to have a structure related to that of the low-pressure phase, while the denser species has a structure related to the denser high-pressure phase which invariably terminates a negative melting slope. The large initial volume change and large entropy of melting of NH_4HF_2 suggest that the liquid at low pressures may even involve a third, very much less dense, species. The liquid near 40 kbar, on the other hand, should contain an appreciable fraction of a species related to NH_4HF_2 III. It is difficult to avoid the conclusion that this dense phase must be a structural rearrangement which still involves hydrogen bonding between the ammonium and FHF^- ions, since the more ionic phases of the alkali metal bifluorides are less densely packed than NH_4HF_2 I (*18*).

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