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# Note on the Phase Transition II'-IV in the Ammonium Rich End of the Mixed Crystals Series $(\text{NH}_4)_x\text{K}_{1-x}\text{NO}_3$

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With 3 figures in the text

## Abstract

The transition curve II'<sub>A</sub>-IV<sub>A</sub> in the range  $\text{NH}_4\text{NO}_3$ - $(\text{NH}_4)_{0.75}\text{K}_{0.25}\text{NO}_3$  was determined. A single phase II' of ammonium rich mixed crystals was observed in the complete miscibility range from  $x=1$  to 0.918 ( $x$  = molar fraction of ammonium nitrate). From  $x=0.913$  to 0.750 two phases occur simultaneously: II'<sub>A</sub> ammonium rich and II<sub>K</sub> as undercooled potassium rich phase. The stable phase at room temperature III<sub>A</sub> forms readily on cooling. The complete miscibility range of phase III<sub>A</sub> extends over the whole range studied here. Hence homogenization of the formerly unmixed crystals sets in, by ion diffusion in the solid state.

## Zusammenfassung

Die polymorphen Umwandlungstemperaturen II'<sub>A</sub>-IV<sub>A</sub> wurden in der Mischkristallreihe  $\text{NH}_4\text{NO}_3$ - $(\text{NH}_4)_{0.75}\text{K}_{0.25}\text{NO}_3$  bestimmt. Am ammoniumreichen Ende wurde eine homogene Kristallphase II'<sub>A</sub> beobachtet, die sich über den Interwall  $x=1$  bis 0,918 erstreckt ( $x$  = Molarfraktion des Ammoniumnitrats). In dem Bereich  $x=0,918$  bis 0,750 werden zwei nicht mischbare Phasen beobachtet, und zwar: II' als ammoniumreichere und II<sub>K</sub> als kalireichere Phase. Die stabile Phase III<sub>A</sub> bildet sich beim Abkühlen auf Zimmertemperatur leicht. Bei dieser Phase erstreckt sich die vollständige Mischbarkeit über den ganzen, hier untersuchten Bereich. Deshalb tritt sofort nach der polymorphen Umwandlung die Homogenisierung der vorher entmischten Phasen auf durch Ionen Austausch im festen Zustande.

## INTRODUCTION

The complete phase diagram of the two-component system  $\text{NH}_4\text{NO}_3$ - $\text{KNO}_3$  was studied by WALLERANT (1905). The literature on the metastable transitions in this system is not abundant. Important studies on  $\text{KNO}_3$  were made by KRACEK (1930), MIEKK-OJA (1946), SAWADA, NOMURA and FUJII (1958), SAWADA, NOMURA and ASAO (1961) and SHINNAKA (1962). The mixed crystals

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of the potassium rich end of the system had been dealt with by YANAGI and SAWADA (1963) and KAWABE, YANAGI and SAWADA (1965). The II'-IV transition of  $\text{NH}_4\text{NO}_3$  was studied by BOWEN (1926), HENDRICKS, POSNJAK and KRACEK (1932), AMOROS, ALONSO and CANUT (1958), SHINAKA (1956 and 1959). See also M. DE SÁENZ, TESSORE and LEONE (1970, this volume).

The influence of  $\text{KNO}_3$  on the II'-IV transition of ammonium nitrate has, to our knowledge, not been submitted to study. TESSORE (1965) observed a transition temperature of  $41 \pm 1^\circ \text{C}$  for  $x = 0.94$  (personal communication). The nomenclature used at present for the different modifications of ammonium and potassium nitrate is given in the sketch of the phase diagram (fig. 1). The suffix A or K is used to differentiate phases, which have the same denomination in the K rich end or the ammonium rich end, by their crystallographic properties (e.g. II<sub>A</sub>-tetragonal and II<sub>K</sub>-rhombic).

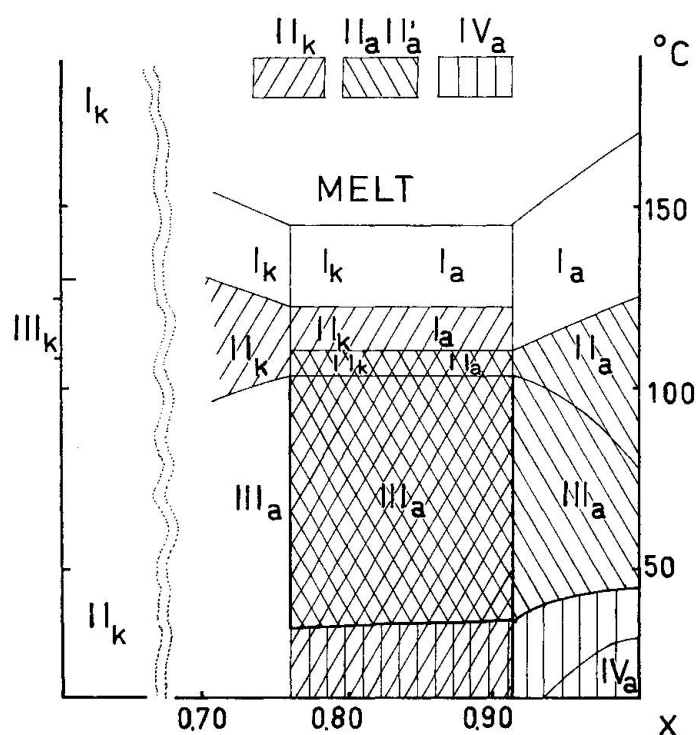


Fig. 1. Stable phase diagram of the system  $\text{NH}_4\text{NO}_3$ - $\text{KNO}_3$  at its ammonium rich end according to WALLERANT including some data from KRACEK; EARLY and LOWRY and from YANAGI and SAWADA. The names of the stable phases are given in the diagram, the limits of the stability fields of the stable phases are drawn with thin lines. The striated areas represent the occurrence of each phase in the metastable phase diagram, as determined in this paper. The names of the phases are given at the top of the graph. Transition curves belonging to the metastable phase diagram are drawn in thick lines. (For more details on the metastable potassium rich phases see YANAGI and SAWADA, 1963.)

#### EXPERIMENTAL

Determinations were made with the Dialux polarizing microscope (Leitz) using the thermostatic heating stage (Leitz 1437). Samples of different composition were prepared by dissolving proportional quantities of both compounds in distilled water ( $\text{NH}_4\text{NO}_3$  Merk A. R. or Prolabo Rhône-Poulenc P.A.). The maximum absolute error in the molar fraction  $x$  of  $\text{NH}_4\text{NO}_3$  in the mixture of both salts was 0.0005. A drop of the solution was evaporated on a microscope slide and fused rapidly on a heating stage at  $170^\circ \text{C}$ . It was then

transferred to the thermostatic heating stage of the microscope and allowed to cool down to  $60^\circ\text{C}$ . The temperature of the stage was noted. The maximum estimated error in the determination of the transition temperature is  $\pm 2^\circ\text{C}$ .

## RESULTS

The graph given in fig. 2 represents the transition temperatures of the  $\text{II}'_{\text{A}}\text{-IV}_{\text{A}}$  transition of the ammonium rich phase. An inflection is observed at  $x = 0.918$  dividing the graph into two zones: the zone of complete miscibility for phase  $\text{II}'_{\text{A}}$  up to  $x = 1$ , and the zone of partial miscibility where  $\text{II}'_{\text{A}}$  coexists with  $\text{II}_{\text{K}}$ . In this range the composition of the ammonium rich phase changes only very little with the total increase of K content of the system. At the

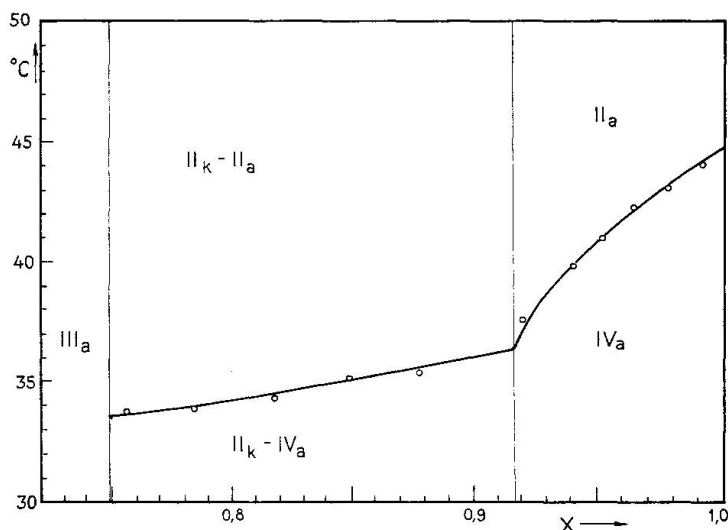


Fig. 2.  $\text{II}'\text{-IV}$  transition curve for the ammonium rich phase in the system  $(\text{NH}_4)_x\text{K}_{1-x}\text{NO}_3$ . A considerable difference is noted in the slope of the complete miscibility area and that of partial miscibility.

temperatures given in the graph, phase  $\text{IV}_{\text{A}}$  forms with the same composition as formerly  $\text{II}'_{\text{A}}$ . Almost immediately unstable phase IV transforms into the stable phase  $\text{III}_{\text{A}}$  and immediately the undercooled potassium rich phase will be found to transform as well. By this procedure, in the compositional range  $x = 0.918$  to  $x = 0.750$  two types of crystals of modification  $\text{III}_{\text{A}}$ , having different compositions, will form. (It is not surprising that the potassium rich phase should only transform after the ammonium rich one does so. As  $\text{II}_{\text{K}}$  transforms only with difficulty into  $\text{III}_{\text{A}}$  it can be considerably undercooled below its range of stability. As soon as the transition  $\text{IV-III}$  occurs in the ammonium rich phase, its crystals act like seeds, causing the immediate transformation  $\text{II}_{\text{K}}\text{-III}_{\text{A}}$ .)

Phase  $\text{III}_{\text{A}}$  is however completely miscible in the compositional range studied here. Under the microscope it can be observed how homogenization of the formerly unmixed crystals sets in and proceeds by diffusion. As the change in composition is accompanied by a considerable change in the refractive in-

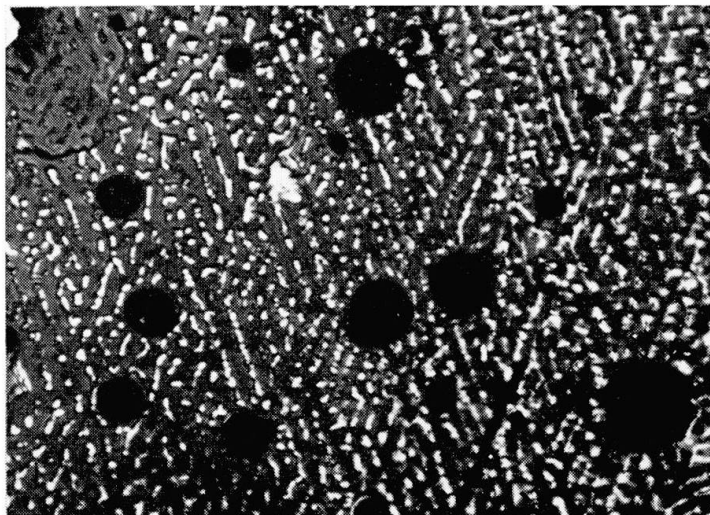


Fig. 3a. Crystals  $II_K$  (light coloured) and  $II_A$  (dark) cooled metastably down to  $60^\circ\text{C}$ .  $x = 0.85$ , partial miscibility range (compare fig. 1). The black spots are air bubbles taken as reference.

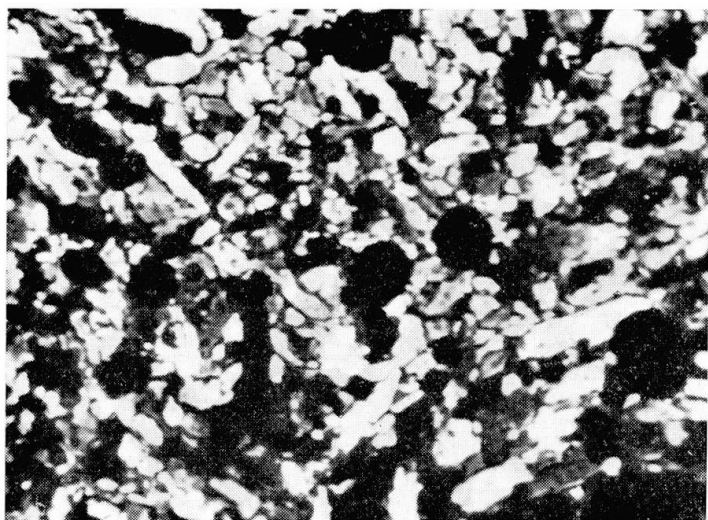


Fig. 3b. The crystal transformed into the completely miscible phase  $III_A$  stable at that temperature. The outlines of the crystals are somewhat diffuse owing to changes in the refractive index in the homogenization of the formerly unmixed crystals and also to the very rapid recrystallization.

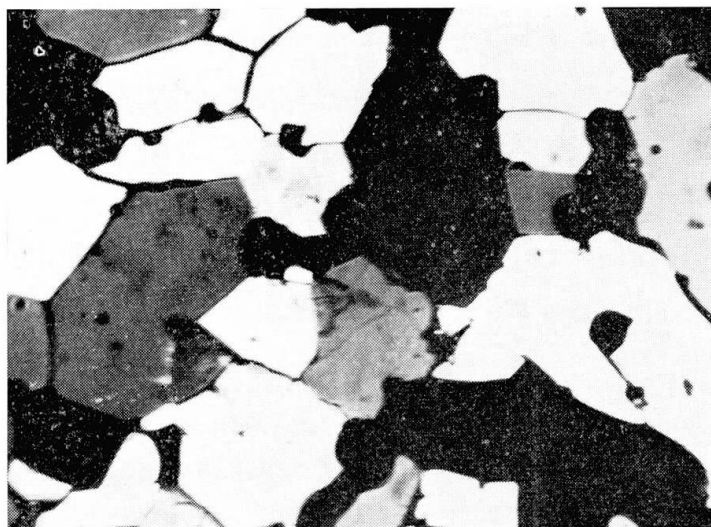


Fig. 3c. The same zone after annealing at  $80^\circ\text{C}$  for 18 hours. The now uniform crystals have developed nearly idiomorphic outlines and have grown considerably in size. (Width of the photographs: 0.5 mm.)

dices and birefringence, the whole sample has the aspect of a stirred liquid. Owing to considerable ion mobility recrystallization starts also immediately, and after some length of time rather large idiomorphic crystals of phase  $\text{III}_A$  will have grown.

As observed above, the presence of  $\text{III}_A$  formed from  $\text{II}_K$  will also act as a seed causing the direct stable transition  $\text{II}_A$ - $\text{III}_A$  to occur. This happens if the sample is maintained for some length of time in the stability range of  $\text{III}_A$ .  $\text{II}_K \rightarrow \text{III}_A$  will occur and  $\text{II}_A \rightarrow \text{III}_A$  follows immediately. In this case the transition  $\text{II}'_A$ - $\text{IV}_A$  cannot, of course, be observed. Under the microscope the two transitions of either example are seen to expand as circular fronts over the slide. Usually the stable transition follows close behind the metastable one. The cooling speed is important in regulating the relative rate of both transitions. From the phase diagram in fig. 1 it could be expected not to meet at all phase IV for the higher K concentrations. As just explained, it is however observed that phase IV forms metastably. This fact can easily be explained by the similarity of the structures of  $\text{II}_A$  and  $\text{IV}_A$ . Certainly the ease of crystallization of phase  $\text{IV}_A$  from  $\text{II}_A$  is much greater than that of the rather complex structure of  $\text{III}_A$ . Thus it is not surprising to find this modification outside its stability range (compare GOLDSMITH, 1955).

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\*) For other references see M. de SÁENZ, TESSORE and LEONE (1970, this volume).