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STUDY ON THE γ–δ PHASE TRANSITION OF ND_4Br CRYSTAL *

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ABSTRACT

Thermal properties of the first-order $\gamma-\delta$ phase transition in ND_4Br crystals were studied by the use of a DTA apparatus. The transition point was systematically dependent upon the prehistories of the sample. The transition temperature in the cooling runs varied by as much as 5.9 K depending upon different thermal treatments. The transition could be stopped halfway at any stage, and also be partitioned into two peaks on a DTA display by devising an appropriate thermal cycling. The changes of the relative magnitude of the two peaks with temperature rise and with time were examined and discussed in relation to the shift in the transition temperature region.

INTRODUCTION

Phase transitions are thermodynamically classified after Ehrenfest in terms of the lowest-order partial derivative of the free energy that exhibits a discontinuity at the transition point [1]. First-order transitions show discontinuities in some properties such as volume, entropy and spontaneous polarization. Two different phases co-exist at the transition point in equilibrium with each other. This situation necessarily gives rise to the kinetic problem of nucleation and growth of the new phase.

The nucleation is in most cases dependent on the structure of the crystal [2]. This is because the embryo of a new phase usually emerges at some defect site. If the sample consists of many crystallites having different defect properties and therefore different nucleation temperatures, the transition occurs over some temperature or pressure range, not complying with the simple phase rule. It sometimes becomes difficult to define the equilibrium transition point.

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The growth process is, on the other hand, affected by the interfacial energy related to the domains of the phases in the free energy expression [1]. In the relatively simple case where the contribution of such a term is negligible as in crystallization or melting, the equilibrium transition point can be clearly defined because the reaction or phase change proceeds with time until the equilibrium state under the given conditions is attained. In the opposite case, as in martensitic materials, the transition is forced to stop at some stage and the completion of the process can be obtained only by the change of external parameters, e.g., temperature, pressure and so on, but not by the elapse of time [3]. Defining the equilibrium transition point becomes quite a difficult problem because of the inevitable appearance of the hysteresis and of the width of the transition temperature.

Deuterated ammonium bromide (ND_4Br) exists in three (β, γ, and δ) phases below room temperature at low pressures [4,5]. The β phase has the CsCl structure, NH_4^+ tetrahedra being in the disordered state distributed over two possible orientations in the octahedral crystal environment made by Br^- ions. Decreasing the temperature changes the β phase into the γ phase through the anti-parallel ordering of the mutual orientation of nearest-neighbor tetrahedra within the ab plane, accompanied with an anti-parallel displacement of the adjacent Br^- ions. A further decrease in temperature causes the crystal of the γ phase to change into the δ phase in which NH_4^+ tetrahedra are arranged in a parallel long-range ordering in the CsCl-type lattice and therefore all three axes are equivalent again.

The δ to γ phase transition is necessarily of the first order because the two types of long-range ordering in the δ and γ phases can not co-exist in the homogeneous crystal. In other words, the δ and γ phases can never transform continuously into each other. In fact, a marked hysteresis associated with this δ–γ phase change in NH_4Br was observed by Stephenson and Adams [6], and Sorai et al. [7] with heat capacity measurements. The transition temperature was about 78 K on cooling and about 108 K on warming. Bonilla et al. [8] measured the temperature dependence of lattice parameters by means of an X-ray diffraction on NH_4Br. However, most of the previous studies on the first-order transitions have been limited to the observation whether there exists or not a hysteresis effect.

The object of this study is to investigate the detailed kinetic behavior of the γ–δ phase transition by means of differential thermal analysis (DTA). The deuterated crystal ND_4Br was used because its γ–δ phase transition takes place at a higher temperature than that of the normal compound, thus enabling us to work with liquid nitrogen as the coolant instead of liquid hydrogen or helium.

EXPERIMENTAL

An ND_4Br sample prepared previously [9] was used in this DTA study. A detailed description of the DTA apparatus used here has already been given [10]. A DTA tube was loaded with the sample in an atmosphere of dry nitrogen gas and then sealed after the nitrogen was replaced by about half an atmosphere of dry helium gas. The heating and cooling rates in the measurement were usually chosen to be about 2 K min^{-1}. Annealing of the sample at some constant temperature was carried out by the use of an electric device of proportional controlling type within the fluctuation of 0.1 K. The error of the temperature setting in reversing the heating and cooling was estimated to be smaller than 0.2 K and the precision of temperature determination to be better than 0.1 K.

RESULTS AND DISCUSSION

Hysteresis in the γ–δ phase transition

The γ–δ phase transition is known to be first order. This character sometimes means that the transition temperature to be observed is quite vague from run to run depending on the prehistory of the sample, the rate of temperature scan, and so on. Figure 1 shows the prehistory dependence of the transition point in the cooling direction. Run 1 was started at room temperature after annealing for a few days. It gave a transition point of 153.48 K. Run 2 was obtained on the sample annealed for 4 h at 156.3 K on the way of Run 1 and heated to 178.1 K. The transition temperature was increased slightly to 154.44 K by this annealing. The effect of annealing on the transition point will be discussed later. In Run 3, the temperature range was the same as in Run 2 but the sample had already undergone the $\delta \rightarrow \gamma$ transition just before the run. The $\gamma \rightarrow \delta$ transition took place at 157.76 K in this run, an increase of 4.3 K above the transition temperature of Run 1. In Run 5, which repeated the same cycling as Run 3, the transition temperature increased further to 158.23 K. However, the highest transition temperature, 159.4 K, was observed in Run 4 in which the temperature was reversed at 171.5 K. This was the temperature at which the $\delta \rightarrow \gamma$ transition was complete, as the heating curve between Run 3 and Run 4 in Fig. 1 shows.

It is concluded that the $\gamma \rightarrow \delta$ transition takes place at a higher temperature, the lower the starting (namely, reversing) temperature of the cooling run. The largest difference found was 5.9 K. The temperatures were read as the rising point of the peak, as shown in Fig. 1. The shape of the peaks was essentially the same with only a shift in the temperature.

The corresponding curves in the heating direction are drawn in Fig. 2. In

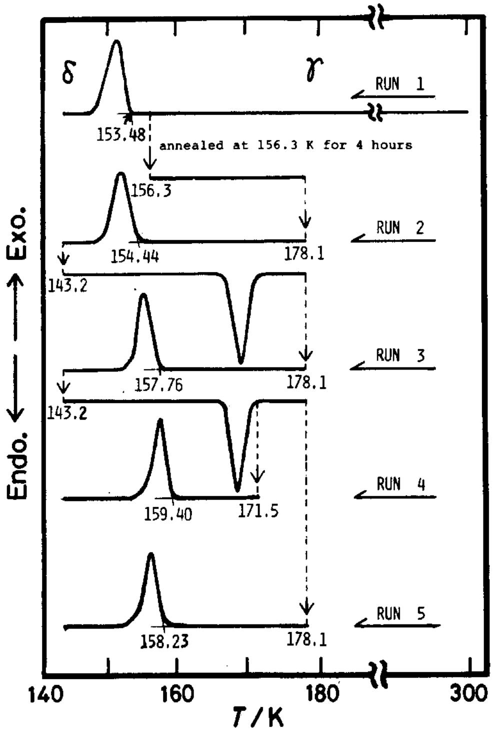

Fig. 1. Thermal-pretreatment dependence of the γ → δ transition temperature of ND_4Br crystals.

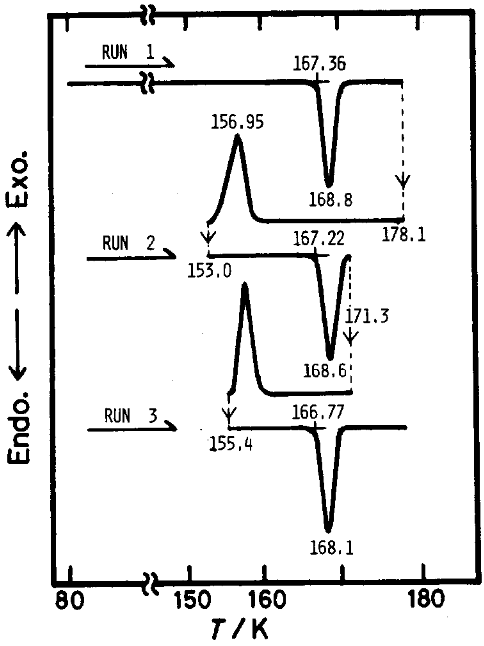

Fig. 2. Thermal-pretreatment dependence of the δ → γ transition temperature.

Run 1, the sample heated from liquid nitrogen temperature underwent a transition at 167.36 K. The transition appeared at 167.22 K in Run 2 which was taken after heating to 178.1 K in Run 1 and subsequent cooling to 153.0 K. Heating of Run 2 was stopped at 171.3 K just above the $\delta \rightarrow \gamma$ phase transition region and allowed to cool to 155.4 K and then Run 3 was begun at that temperature. The transition temperature of 166.77 K is lower by 0.6 K than that of Run 1, indicating that the transition occurs at a lower temperature, the higher the reversing point from cooling to heating is.

Partition of the transition peak

It is evident from Fig. 1 that the transitional behavior of the $\gamma \rightarrow \delta$ phase change can be very different from run to run depending on the sample's thermal history. In this section the following peculiar property of the present transition is described. The transition could be stopped in the middle stage depending on the lowest or highest temperature in the transition region during temperature cycles and, furthermore, the transition peak could be partitioned into two.

Figure 3 shows example curves. Run 2 in Fig. 3(a), reversed and started at 155.9 K in the middle of the $\gamma \rightarrow \delta$ phase transition in Run 1, was heated to 178.1 K. The peak found there was small in its area in comparison with that in Run 0. Also, in Run 3 where the cooling was started at 165.9 K just below the transition point in Run 2, the peak was considerably reduced in contrast with that in Run 1 in the same cooling direction. The transition point of 156.8 K is close to 155.9 K, the reversing point before Run 2, rather than to

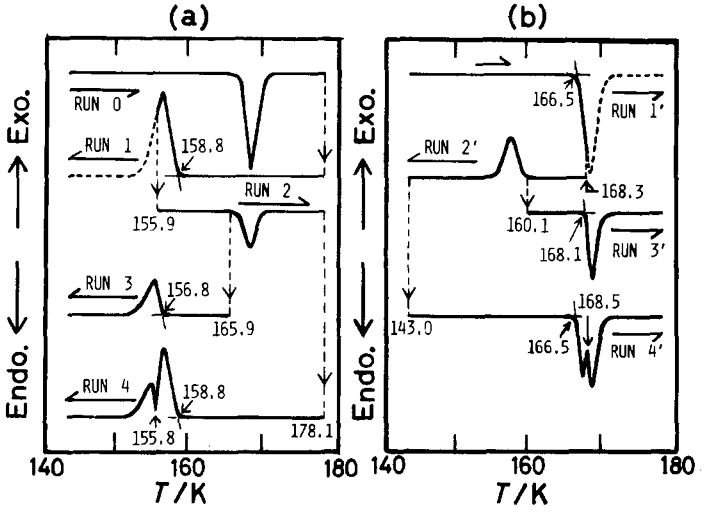

Fig. 3. Metastability of the crystalline state in the middle stage of the $\gamma \rightarrow \delta$ and the $\delta \rightarrow \gamma$ phase transition, and partition of the transition peak into two parts.

158.8 K, the rising temperature in the curve for Run 1. The peak in Run 2 is due to the $\delta \rightarrow \gamma$ phase transition in that part of the sample which has transformed into the δ phase above 155.9 K in Run 1, while that in Run 3 is due to the other part which has remained in the γ phase at temperatures above 155.9 K in Run 1.

Run 4 shows the cooling curve started at 178.1 K after Run 2. There are two peaks with the first rising temperature at 158.8 K and the second at 155.8 K. The latter temperature is essentially the same as the temperature, 155.9 K, at which cooling Run 1 was reversed to heating Run 2. Apparently, the crystal "remembered" that the temperature was reversed in the middle of the $\gamma \rightarrow \delta$ phase transition even after it had transformed into the original γ phase in Run 2.

Figure 3(b), on the other hand, shows the corresponding curves for the $\delta \rightarrow \gamma$ phase transition. The transition can be stopped and kept in the halfway point as in the $\gamma \rightarrow \delta$ transition.

Figure 4 shows that the phase transition can be stopped at any stage halfway in the transition region. The experiment of reversing the direction of temperature change into heating on the way of cooling through the transition region was carried on the sample which had just experienced the δ phase as shown in Run 3. The temperatures reversed in Run 3 were 157.3, 156.3 and

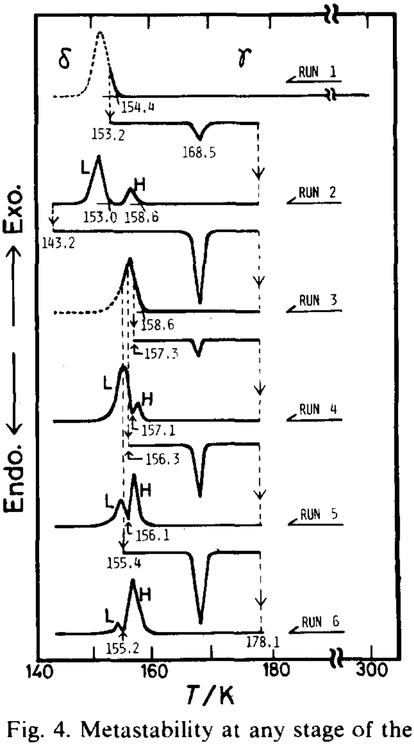

Fig. 4. Metastability at any stage of the $\gamma \rightarrow \delta$ transition with different reversal temperatures in the transition region.

155.4 K to obtain the curves for Runs 4, 5 and 6, respectively. The ratio in area of peaks L and H became smaller as the reversal temperature was lowered.

Relative magnitude of the two peaks

Figure 5 shows the observation concerning a partitioning of the $\gamma \rightarrow \delta$ phase transition peak into two covering wider temperature regions. In this experiment the highest point in a temperature cycle prior to each of Runs 1–5 was changed from run to run while keeping the reversal temperature constant at 156.3 K. Run 1 was taken in the cooling direction after heating from 145 to 171.5 K and the temperature cycle between 171.5 and 156.3 K. The temperature 171.5 K is just above the end point of the $\delta \rightarrow \gamma$ phase change in the heating direction. The highest temperatures in Runs 2–5 were 178.1, 199.2, 216.1 and 219 K, respectively, the last two being chosen as points just below and above the $\gamma \rightarrow \beta$ phase transition temperature.

Cooling curves 1–5 exhibited a systematic change in the shape of two

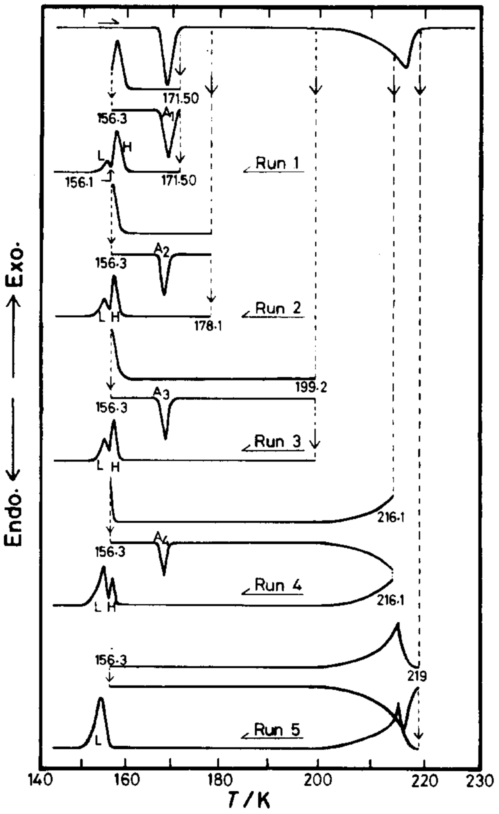

Fig. 5. DTA curves of the $\gamma \rightarrow \delta$ phase transition in ND_4Br crystals with different highest points in temperature cycles.

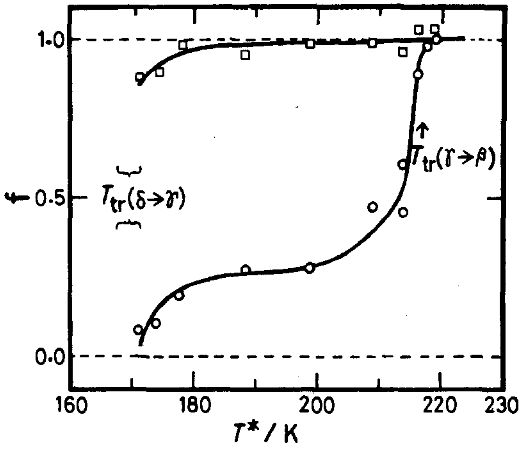

Fig. 6. Dependence of the relative magnitude of the two $\gamma \to \delta$ transition peaks on the highest temperature T^* in a temperature cycle.

peaks. The two peaks L and H at the partitioning temperature 156.1 K may be separated, and the respective peak areas designated S_L and S_H. Both the ratio of the total area, $(S_L + S_H)$, to that in Run 1 of Fig. 4 and the ratio of the lower-temperature peak area S_L to the total area are plotted with the symbols □ and ○ in Fig. 6, respectively, against the highest point T^* in each temperature cycle. Solid lines are for guidance.

The slight deviation of the □ plot from unity at lower temperatures ($T^* \approx 170 \sim 180$ K) indicates that a small part of the crystal remained in the δ phase at these T^* temperatures at which the γ phase is nominally the most stable. On the other hand, the ○ plot shows that the relative importance of the two peaks depends substantially on the temperature T^*. As T^* increases, an increasing portion of the crystal undergoes the $\gamma \to \delta$ phase transition at the lower of the two peak temperatures. However, the relationship is not regular as Fig. 6 shows. The slope of the ○ curve is large around 173 K just above the $\delta \to \gamma$ transition and around 216 K just below the $\gamma \to \beta$ transition. The former would be related to the T^*-dependence of the total peak area (□) plotted in Fig. 6. The latter shows that the $\gamma \to \delta$ transition is influenced in its hysteretic behavior by the $\gamma \to \beta$ phase transition.

Effect of annealing on the γ to δ phase transition

The effect of isothermal annealing was studied next. The results are summarized in Fig. 7. The sample was annealed at 156.3 K in the middle of the $\gamma \to \delta$ transition. Annealing time was zero for Run 2, 5 h for Run 3 and 21 h for Run 4. As the annealing time increased, the peak occurring at the lower temperature in the subsequent cooling run decreased slightly in its magnitude. This means that some parts of the sample, being in the under-

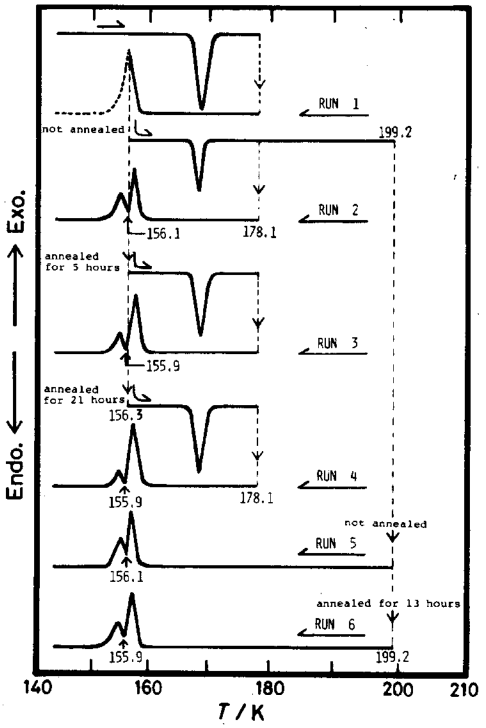

Fig. 7. Effects of isothermal annealing at 156.3 K on the $\gamma \rightarrow \delta$ transition region and at 199.2 K on relative magnitude of the two peaks in the subsequent DTA curves of the transition.

cooled γ phase at 156.3 K, transformed into the δ phase during the isothermal annealing at that temperature.

In relation to this, the effect of annealing at the same temperature 156.3 K carried out between Runs 1 and 2 of Fig. 1 is of interest. The transition temperature in Run 2 was observed at 154.4 K, higher by 1 K than that in Run 1, in spite of the fact that the annealing temperature was ~ 3 K higher compared with the transition point in Run 1. Evidently, no part of the crystal changed from the γ to the δ phase during the annealing at 156.3 K because there was no endothermic effect in the subsequent heating run to 178.1 K. Nevertheless the annealing had a destabilizing effect on the γ phase as is evident from the 1.0 K upward shift of the transition temperature in Run 2 from that in Run 1. This point will be mentioned later again concerning the nucleation and growth processes.

Runs 5 and 6 of Fig. 7 show the effect of annealing at 199.2 K with an annealing period of 13 h for the latter. At this temperature the γ phase is stable, contrary to the above cases in Runs 2–4. The annealing gave rise to a small downward shift in temperature of the minimum between the two peaks.

Figure 8 shows the effect of annealing at 300 K at which the β phase is

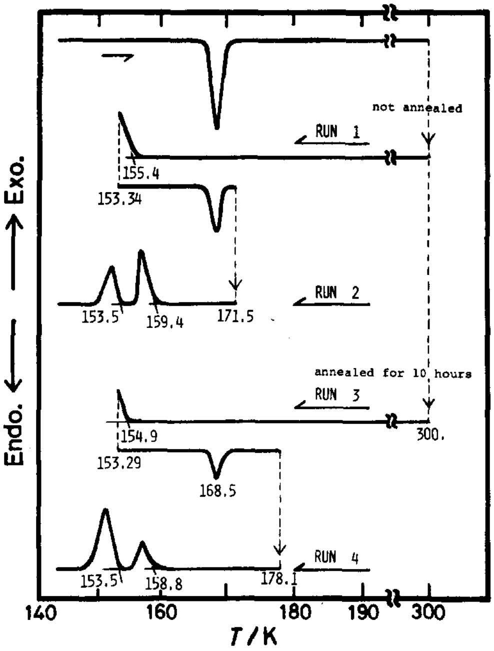

Fig. 8. Effect of annealing at 300 K at which the β phase is stable. A clear difference is seen in the relative magnitude of the two peaks between Runs 2 and 4.

stable. Annealing for 10 h brought about a big difference in the ratio between the areas of the two peaks associated with the $\gamma \rightarrow \delta$ phase change, as drawn in Runs 2 and 4. This is attributed to a change in the transition temperature region as a whole by the long annealing process. Apparently, the crystal "remembered" that it had experienced the $\gamma \rightarrow \delta$ phase transition at lower temperatures even after it was brought back to room temperature. The "memory" was partly erased by annealing at 300 K for 10 h and would be erased completely if a long period of time elapsed. The $\gamma \rightarrow \delta$ transition temparature 154.9 in Run 3 is still 1.4 K higher compared with that in Run 1 of Fig. 1.

Origin of the transition temperature region and its shift by prehistory

As described above, the $\gamma \rightarrow \delta$ phase transition apparently could be stopped at the halfway stage, could be partitioned into two peaks by applying a certain thermal pretreatment, and was distinctly influenced in its hysteretic character by annealing. These peculiar observations are attributed to the presence of a temperature region within which the transition could occur at any point (this is not allowed in the usual thermodynamics of bulk phases), and to the systematic shift in the region by prehistory.

Suppose that different parts of the sample had different nucleation temperatures. Then we might expect that the part of the γ-phase sample which has a higher nucleation temperature than the others will transform into the δ phase at a higher temperature. If the cooling is stopped when a fraction of the sample has changed to the δ phase, a mixture of the γ and δ phases will be obtained so long as the temperature is kept below the $\delta \rightarrow \gamma$ transition temperature ($\simeq$ 167 K). Once transformed, that part of the crystal will be different from the original one in its nucleation temperature, interfacial coherence with neighboring regions and strain within itself. This explains the splitting of the peak due to the $\gamma \rightarrow \delta$ phase transition. The difference between the transformed and original crystals disappears with the elapse of a long period of time at higher temperatures, especially above the $\gamma \rightarrow \beta$ phase transition point.

In addition to the effect of the coexistence of the phases, there is a destabilizing effect of annealing on the single phase, as discussed above in relation to Runs 1 and 2 of Fig. 1. They showed that annealing of the single γ phase at 156. 3 K destabilized it in the subsequent cooling run. This may be called an incubation effect which prepares the metastable γ phase for ready transformation into the δ phase in a subsequent cooling [1]. The physical meaning of the incubation period is not clear at present.

CONCLUSIONS

The present study disclosed novel phenomena relating to the $\gamma \rightarrow \delta$ phase transition in the ND_4Br crystal. They are basically due to the variation in the hysteresis of the undercooling and superheating characteristics of the first-order phase transition. The apparent transition took place within a certain temperature region which was systematically dependent on the prehistory. It was earlier reported that the δ to β transition line continued into the γ-phase region near the β–γ–δ triple point in the p–T phase diagram of ND_4Br [9]. This behavior is explained by superheating of the δ phase if it is assumed that it occurs at a higher pressure as well.

There have been occasional descriptions of metastability and suspended transitions ($K_4Fe(CN)_6 \cdot 3\ H_2O$ [11], $(NH_4)_3FeF_6$ [12], $(CH_3NH_3)_2TeCl_6$ [13]). In all of these examples the phase transition can be stopped at any stage if the temperature is changed appropriately. The two phases coexist thereafter over a limited temperature region, in obvious contradiction to bulk thermodynamics. In fact, a generalized theremodynamic formulation has been proposed [14]. At present, however, we cannot make a specific prediction on a given substance because we do not know the physical nature of the agency which determines the stability and metastability of the substance. In the present study, a new aspect of the metastability—splitting of the phase transition—was discovered and studied in detail. This should help in a general understanding of the non-classical behavior of first-order transitions in a more systematic way.

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