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# Phase Transitions in the (Ni,Zn)$TiF_6 \cdot 6H_2O$ System

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Measurements of the transformation rates and the characteristic temperatures of the trigonal ↔ monoclinic structural change in $(Ni_{1-x}Zn_x)TiF_6 \cdot 6H_2O$ show a double transition up to $x = 0.5$. The relationships between the phase changes generally observed in the $ABF_6 \cdot 6H_2O$ system and the internal motions of the octahedral ionic complexes are discussed, and a phase diagram for the mixed nickel/zinc fluorotitanate is established.

## Introduction

Structural phase transitions in the $ABF_6 \cdot 6H_2O$ system ($A$ is a 2+ 3$d$-ion and $B$ is a 4+ ion) have been investigated for nearly 20 years. Recent detailed studies (*1–5*) have shown this system to be considerably more complicated than was previously understood. The fluorotitanates, in particular, have been shown to have more than one structural change (*2, 4, 5*). Although these complex ionic salts are nominally isostructural, there are numerous differences in the details of the structures and the nature of the phase transitions among members of this group.

The basic structure is a slightly distorted CsCl-type packing of the $[A(H_2O)_6]^{2+}$ and $[BF_6]^{2-}$ octahedral ions additionally linked by 12 O–H. . .F hydrogen bonds per chemical unit. Near room temperature and above, the structures belong to either the $R\bar{3}$ or $R\bar{3}m$ groups with a single chemical unit per primative cell. Substantial rotational reorientation of the octahedral substructures and the water molecules exists in this phase. At low temperatures where these motions are absent the structure of most of these salts is more consistent with a monoclinic assignment having two chemical units per cell.

The change from trigonal symmetry with rapid reorientational motions to monoclinic symmetry without these motions apparently takes place in several steps, presumably related to the freeze-out of various modes and the associated modifications to the hydrogen bonding patterns. Results of $^2H$ NMR studies (*4*) indicate a rearrangement of the hydrogen bonds while the overall structure remains trigonal. In addition, at the same temperature the dynamics of reorientational motions change as might be expected from a change in the weak hydrogen bonds between the basic structural units. This transition has been found in most of the fluorotitannates and in several of the fluorosilicates, and takes place over a narrow temperature range in most cases. The primary trigonal to monoclinic trans-

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formation is first order and involves an antiferrodisplacive rotation of the octahedral complexes leading to a doubling of the unit cell. This reorientation may be accompanied by distortions of one or both the hydrated metal and fluoride octahedra.

In the case of $NiTiF_6 \cdot 6H_2O$, the disappearance rate of the supercooled trigonal phase as monitored by $Ni^{2+}$ ESR (*1*) shows two separate critical temperatures (near 136 and 126 K) associated with the trigonal to monoclinic transformation. Additionally, $^1H$ and $^{19}F$ NMR linewidth studies (*2*) show independent steps at these two temperatures, implying that distortions of the two octahedra take place slightly separated in temperature. The NMR linewidths also show a higher temperature transition near 204 K as an anomalous decrease in the $^1H$ width over a 2–3 K region and an abrupt change in the width versus temperature slope for $^{19}F$. A similar change in the fluoride dynamics is seen at 217 K in the 50% Zn sample. This transition should probably be associated with the ones observed by $^2H$ NMR mentioned above, since the symmetry remains trigonal in both cases.

In order to investigate the extent to which the trigonal to monoclinic transformation is a double transition, we have studied the mixed $(Ni,Zn)Ti_6 \cdot 6H_2O$ system using the transformation rate measurements which originally showed separate critical temperatures. Here we report results of those experiments for Zn concentrations up to 50%, and measurements of the characteristic temperatures for the recovery of the trigonal phase upon reheating for the full concentration range.

## Experiments

The procedures followed for the rate measurements were the same as those reported in detail for the pure Ni salt (*1*). Basically we cooled very rapidly through the critical region, stabilized at a given temperature, and monitored the time dependence of the disappearance of the $Ni^{2+}$ ESR signal from the trigonal phase. This type of measurement is limited to systems where the transformation rate is slow enough to allow the cooling and temperature stabilization to be accomplished before the transition has proceeded significantly. In analyzing the data, the time constant for the exponential tail of the transformation is assigned to the growth phase of a slow-nucleation/rapid-growth model. The temperature dependence of the growth rate constant K yields the critical temperature $T_c$, the barrier height $E$ for adding a chemical unit to the growing phase, and the heat of transformation $Q$ when fit using a simple double well potential picture. Specifically, this temperature dependence is given by

$$K = A \exp\left[\frac{3E}{kT}\right]\left\{1 - \exp\left[\frac{Q}{k}\left(\frac{1}{T_c} - \frac{1}{T}\right)\right]\right\}^3, \tag{1}$$

where $A$ is a multiplicative constant which includes the nucleation rate information.

Since the transformation occurs too rapidly at higher Zn concentrations for this procedure to be used, and since the rate measurements require a large number of thermal cycles for each concentration, we also studied the whole concentration range using a much simpler procedure. For this second series of measurements, the transformation to the monoclinic structure was allowed to procede to completion at some temperature well below $T_c$, then while warming at a constant rate (usually 0.5 K/min) the recovery of the trigonal phase ESR line was monitored. The midpoint of the recovery was then taken as a characteristic temperature for the monoclinic to trigonal transition. Note that this procedure identifies only the upper of the two transitions observed with the the other procedure.

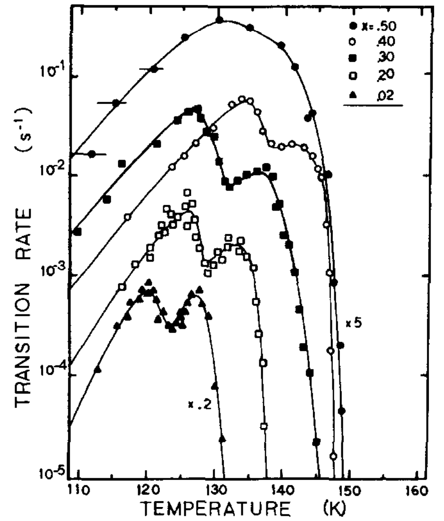

FIG. 1. Temperature dependence of the transformation rates out of the supercooled trigonal phase of $(Ni_{1-x}Zn_x)TiF_6 \cdot 6H_2O$ for several values of $x$. The curves are shifted vertically for clarity.

## Results

Transformation rates for several concentrations of $(Ni_{1-x}Zn_x)TiF_6 \cdot 6H_2O$ are shown in Fig. 1 as a function of temperature. Up to $x = 0.4$ there is a clear indication of two transitions. The curve for $x = 0.5$, while not showing two well-defined peaks, requires two transitions to give reasonable fit parameters. For $x = 0.6$ and 0.7 only a few points on the high temperature side of the curve could be obtained (not shown) since the transformations became too rapid. From these points an estimate of $T_c$ was made, but no determination of the energy parameters was possible. Each peak in these curves was fit to Eq. (1), thus for $x \leq 0.5$ each curve was fit to a sum of two such expressions. When fitting a two-peaked curve, the high-temperature side provides a good determination of the upper $T_c$ while the low-temperature side gives the barrier for the lower transition. The crossover region gives reasonably good values for the upper barrier and the lower $T_c$. The fits are not particularly sensitive to the heat of transformation for either transition. The fit parameters listed in Table I were obtained with $Q$ fixed at 0.66 kcal/mole for both transitions, which was taken from specific heat measurements on the pure Ni salt (*6*). This choice is consistent with the results of our earlier data for $x = 0$ which gave essentially identical values of $E = 5.00$ kcal/mole and $Q = 0.66$ kcal/mole for both transitions (*1*). The quoted values are from fits to samples cut from a single crystal, although the data in Fig. 1 includes points from several crystals in some cases, shifted so the curves overlap. Actual rates varied by up to a factor of ~2.5 between crystals of the same concentration, although each showed identical temperature dependence.

Figure 2 displays the characteristic temperature $T_0$ for recovery of the trigonal phase following a completed transition to the low-temperature structure. This was measured as the midpoint of the recovery of the ESR line intensity. It should be noted that during cooling the steady state was a coexistence of two phases for several degrees below the upper $T_c$ value, and even at the lowest temperatures the trigonal ESR line often remained just detectable. Upon

TABLE I

TRANSFORMATION RATE PARAMETERS

| | Upper transition | | Lower transition | |
|---|---|---|---|---|
| Concentration $x$ | $T_c$ (K) | $E$ (kcal/mole) | $T_c$ (K) | $E$ (kcal/mole) |
| 0[a] | 136.3(.5) | 4.9(0.6) | 126.0(1.0) | 5.0(0.6) |
| 0.02 | 130.9(.6) | 10.0(2.0) | 124.0(1.5) | 8.0(3.0) |
| 0.10 | 134.2(.8) | 7.6(2.4) | 125.5(1.5) | 6.2(2.4) |
| 0.20 | 137.8(.6) | 6.2(1.8) | 130.0(1.5) | 5.0(1.4) |
| 0.30 | 143.6(.8) | 5.2(1.0) | 133.2(1.2) | 4.9(0.8) |
| 0.40 | 147.8(.9) | 4.1(1.8) | 141.2(1.5) | 5.2(1.6) |
| 0.50 | 151 (1.5) | 3.2(1.5) | 146(2) | 3.6(2) |
| 0.60 | 154 (1.5) | — | | |
| 0.70 | 161(2) | — | | |

*Note*. Critical temperatures $T_c$ and the barrier heights $E$ for $(Ni_{1-x}Zn_x)TiF_6 \cdot 6H_2O$ with the heat of transformation fixed at $Q = 0.66$ kcal/mole.

[a] Reference (*1*).

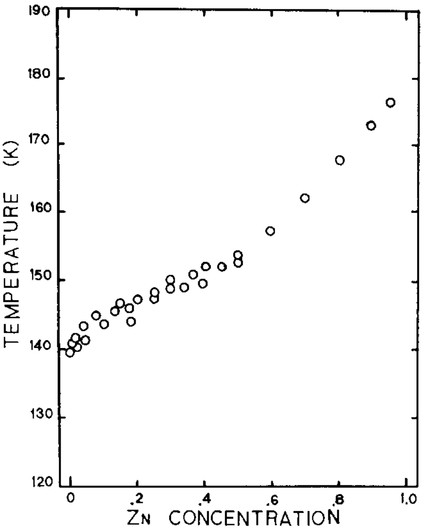

FIG. 2. Characteristic temperatures $T_0$ for the recovery of the trigonal phase upon heating for $(Ni_{1-x}Zn_x)TiF_6 \cdot 6H_2O$ as a function of concentration.

warming this residual intensity began to grow at temperatures comparable to the upper $T_c$ determined from the rate measurements. However, that value was very difficult to accurately define during the heating cycle, hence the adoption of the recovery midpoint as an easily measurable characteristic temperature. Use of these dual procedures gives rise to a "hysteresis" of nearly 10 K at low $x$ decreasing more or less linearly to about 1 K at $x = 0.7$, consistent with other reports of hysteresis in this system (*7*, *9*). The most obvious feature in the $T_0$ vs $x$ curve of Fig. 2 is the kink near $x = 0.6$, which roughly corresponds to the concentration where the separate transitions at low $x$ in the rate measurements become indistinguishable.

## Discussion

The transformation rate measurements reported here clearly indicate that two separate changes occur during the trigonal to monoclinic structural transformation on cooling in the mixed system $(Ni_{1-x}Zn_x)TiF_6 \cdot 6H_2O$ for concentrations up to $x = 0.5$ or 0.6. As discussed in an earlier paper (*1*) on the double transition in pure $NiTiF_6 \cdot 6H_2O$, these measurements actually observe spectral features from only the trigonal phase; thus, they do not establish that a separate structural phase exists in the intermediate region. The results do show that the dynamics of the transformation out of the supercooled trigonal phase undergo an abrupt change several degrees below the onset temperature, observable primarily as a lowered critical temperature. Stronger evidence for a separate intermediate structure is provided by the separate NMR linewidth changes for $^1H$ and $^{19}F$ for the pure nickel salt (*2*) as discussed under Introduction. The combined results presented in this paper suggest that above approximately $x = 0.6$ in the mixed nickel/zinc fluorotitanate the separate changes to the hydrated metal and fluoride octahedra, observed at low $x$, merge into a single structural transition.

The double transformation present below ~150 K in this system for low $x$ values is distinct from the rearrangement of the hydrogen bonding network within the trigonal phase, which was seen by Bose *et al.* (*4*) in deuterated $ZnTiF_6 \cdot 6H_2O$. They report the bond rearrangement at 235 K in the zinc salt; while Cheung and Lichti (*2*) report features, quite likely due to the same source, at 204 K in the nickel salt. Bose *et al.* missed this transition in the deuterated nickel salt because the $^2H$ NMR line was not visible in that temperature region due to the slowing of the 180° flip motions of the $D_2O$ molecule.

When one takes all the available evidence into account a phase diagram for the $(Ni_{1-x}Zn_x)TiF_6 \cdot 6H_2O$ system can be constructed. Figure 3 shows such a diagram along with the data points used to define the various transition lines. Several points (*6*–*10*) are included in addition to the data re-

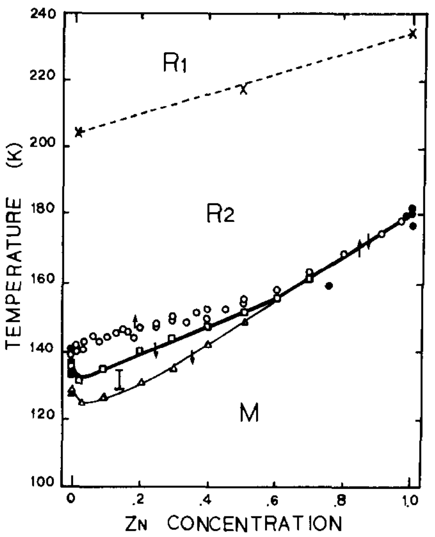

FIG. 3. Phase diagram for $(Ni_{1-x}Zn_x)TiF_6 \cdot 6H_2O$. The dashed line is the hydrogen bond rearrangement transition. The solid lines are the trigonal and monoclinic phase boundaries. Phase labels: R1 and R2 are trigonal, M is monoclinic, I is the intermediate phase of unknown structure. Open symbols are from this work and closed symbols are from Refs. (*6–10*).

ported or discussed in detail here. Much of the spread in the data is due to different experimental techniques and definitions of transition temperature. Taking these differences into account, transition lines have been drawn to represent the critical temperature for the onset of a phase change during cooling. Four different structural phases are identified: two are trigonal (R1 and R2) separated by the hydrogen bond rearrangement, the low-temperature phase is presumed to be monoclinic (M) with a doubled unit cell, and the fourth is the intermediate phase of unknown structure (I) present during the R2-M transformation for low zinc concentrations. The heavy line in Fig. 3 is the lower limit of the purely trigonal structure. The transition out of that phase is of first order with a region of coexistence extending below that line by at least 7 K at $x = 0$ and about 2 K at $x = 1$. From Fig. 3 and Table I one may note that for the initial Zn substitution the critical temperatures for the double transition drop, and then rise roughly linearly with higher Zn concentrations, while the barrier energy initially rises and then falls with increasing $x$.

Combining the above information with knowledge of the internal motions in the $ABF_6 \cdot 6H_2O$ group of complex ionic salts, one may draw the following conclusions. (See also the Discussion in Ref. (*2*) and references therein.) The phase transitions are associated with modifications of the hydrogen bonding network joining the $A(H_2O)_6$ and the $BF_6$ octahedra which make up the basic structure, and with small rotations and/or distortions of the individual octahedra. In the R1 phase rapid reorientation of both octahedra exists, requiring a highly dynamic hydrogen bond network. In the R2 phase reorientational motion of the hydrated metal complex has slowed accompanied by a partial stabilization of the hydrogen bonds, although the rotational motion of the $BF_6$ complex remains quite rapid. At lower temperatures the slowing of the fluoride rotations and the associated additional rigidity of the hydrogen bonds leads to the canting of the octahedral complexes and the doubled unit cell. This transition to the monoclinic phase (in at least some cases) takes place in two steps, the second of which may be a distortion of one or both octahedra. The 180° flip motion of water molecules is present in all the structural phases for at least some of these salts, and thus cannot play any important role in these structural changes, but may be responsible for some of the differences in the transitions observed within this group. Additional differences are likely due to the varying susceptibility of the octahedral complexes to distortion depending on the identity of the $A^{2+}$ and the $B^{4+}$ ions at their centers.

In conclusion, we reported measurements of the transformation rates and the characteristic temperatures of the trigonal ↔ monoclinic structural transformation in the $(Ni_{1-x}Zn_x)TiF_6 \cdot 6H_2O$ system. These results define an intermediate nontrigonal phase for low zinc concentrations. Combined with previous investigations of the end members of this series, these measurements allow the assignment of a phase diagram to this system which consists of four distinctly different structural phases. Additional work remains to define the specific changes associated with the two steps in the trigonal to monoclinic transformation of $NiTiF_6 \cdot 6H_2O$ and low zinc concentrations in the mixed system.

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