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Modification of the phase transition temperature in $ZnTiF_6 \cdot 6H_2O$ single crystals doped with various concentrations of Ni^{2+} and Cu^{2+} probes

Dilip K. De[*]
Department of Physics, The University of Texas at Arlington, Box 19059, Arlington, Texas 76019, USA

J. B. Yerima[†]
Department of Physics, Federal University of Technology, P. M. B. 2076 Yola, Nigeria

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EPR measurements have been carried out on modification of phase transition temperature (T_{c1}) of $ZnTiF_6 \cdot 6H_2O$ single crystals doped with various concentrations of Ni^{2+} and Cu^{2+} ion as probes. It is found that T_{c1} at which the crystal changes from trigonal phase ($R\bar{3}m$) to monoclinic phase ($P2_1/C$) decreases as the impurity concentration increases, the decrease being much greater for the Jahn-Teller Cu^{2+} ion than for the non-Jahn-Teller Ni^{2+} ion. The experimentally observed variation in T_{c1} of Ni^{2+}:$ZnTiF_6 \cdot 6H_2O$ crystals with Ni^{2+} concentration has been explained based on thermodynamic free energy. A good fit between the observed and calculated ΔT_c values as a function of the atomic fraction of Ni^{2+} impurity was obtained. The theory was extended to Cu^{2+} (JT ion) using the same characteristic constants as for Ni^{2+}:$ZnTiF_6 \cdot H_2O$ crystals and introducing modification factor δ due to Jahn-Teller effect. A good fit between the observed and computed ΔT_c values was obtained when δ was allowed to vary slightly with the atomic fraction of Cu^{2+} (x) up to $x=0.0528$, above which the theory practically failed. Probable reasons have been given for the failure beyond $x=0.0528$.

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I. INTRODUCTION

$ZnTiF_6 \cdot 6H_2O$ (ZTFH) belongs to a group of compounds with a general formula $ABF_6 \cdot 6H_2O$, where A is a divalent metal (e.g., Zn and Mg) and B is a tetravalent metal (e.g., Ti, Si, and Ge). Their crystal structure is made up of nearly regular $A(H_2O)_6$ and BF_6 octahedra arranged in a trigonally distorted structure similar to that of CsCl.[1,2] A host of these compounds exhibit first-order structural phase transition in the temperature range 130–300 K, from the high-temperature trigonal phase ($R\bar{3}m$) to the low-temperature monoclinic phase ($P2_1/C$).[1,2]

NMR studies[3] of ^{19}F in ZTFH reveal a first-order phase transition at 182 K (T_{c1}) when the rotation of the fluorine octahedral freezes and the single ^{19}F line splits into two, indicating the loss of a chemical equivalence between the fluorine atoms, followed by a tetragonal distortion of the $[TiF_6]^{2-}$ octahedral. Since at T_{c1} no significant change in the ^1H resonance was observed, they[3] postulated that a change in the $[Zn(6H_2O)]^{2+}$ symmetry caused a sudden transition. A weak transition of a continuous nature at 217 K (T_{c1}) was observed, through the combined infrared, Raman, dielectric and thermal-expansion measurements.[4–7] It was concluded that the weak transition at 217 K was associated with the tilt of the $[M^{2+},H_2O]$ octahedral. An abrupt contraction in the c direction and associated expansion in the a and b directions occurred near 182 K on cooling; sudden drops in the dielectric constant in the b and c directions were found near 194 K on cooling. Das *et al.*[8] theoretically investigated the various coupling between the vibrational and rotational modes of $[TiF_6]^{2-}$ and $[M^{2+},H_2O]$ octahedral. Bose *et al.*'s[9,10] studies of $ZnTiF_6 \cdot 6H_2O$ and deuterated ZTFD crystals confirmed two phase transitions in these materials, with ($R\bar{3}m$) and ($P2_1/C$) symmetry above/below the upper/lower transition and an undetermined intermediate phase.

Cu^{2+} ion in ZTFH has an orbitally degenerate ^2E ground state. De *et al.*'s[11] EPR detailed studies on Cu^{2+} doped ZTFH revealed, as expected, that a Cu^{2+} ion in this system exhibits a strong Jahn-Teller (JT) effect.[12] With a low Cu^{2+} concentration of 0.043% by weight (wt %), the transition temperature T_{c1} was lowered by ∼11 °C from that (182 K) of pure ZTFH; and further lowering in T_{c1} occurred when the crystal was powdered.[13] Rubins *et al.*[14] studied the trigonal to monoclinic phase transition in ZTFH as a function of Mn^{2+} concentration. In contrast to the said lowering of T_{c1}, Mn^{2+} ions increase[14] T_{c1} as observed[15] also in Mn^{2+}:$ZnGeF_6 \cdot 6H_2O$. The origin of such changes remains unexplained.

Earlier we have studied,[16,17] both experimentally and theoretically the dynamics of different impurities (Cu, Zn, and Mn) doped at various concentrations in $CaCd(CH_3COO)_4 \cdot 6H_2O$ single crystals. Each of the impurities modifying phase transition substitutes for Cd^{2+} ion. Even though earlier De *et al.*[11] reported the lowering of T_c in Cu:ZTFH for Cu^{2+} concentration of 0.043 wt %. As continuation of our studies,[16,17] we have carried out EPR measurements of the phase transition temperature T_{c1} (which is 182 K in pure crystal) of ZTFH crystal doped with Cu^{2+} ($3d^9, S=\frac{1}{2}$) or Ni^{2+} ($3d^8, S=1$) ions separately at various concentrations. The study is aimed at revealing the different role of the Jahn-Teller Cu^{2+} ion versus the non-Jahn-Teller Ni^{2+} ion in variation in T_{c1} and the nature of phase changes in ZTFH. We attempt to explain the observed changes in T_{c1} with Ni^{2+} impurity atomic fraction. The theory also explains some changes of T_{c1} with Cu^{2+} concentration up to certain atomic fraction (0.0528). Beyond that a new theory seems to be required to fit the observed data for Cu^{2+} ions with higher atomic fraction (i.e., greater than 0.0528).

TABLE I. Observed changes in the phase transition temperature ($\Delta T_{c1}=T_{c1}-T_{co}$) (°C) in $Ni^{2+}:ZnTiF_6 \cdot 6H_2O$ with varying Ni^{2+} concentration; T_{co} for pure lattice=182 K=−91.2 °C.

Concentration, c wt % ±0.01	Atomic fraction, x	On cooling $\Delta T_{c1}\downarrow = T_{c1}-T_{co} \pm \varepsilon$ (K)	On warming $\Delta T_{c1}\uparrow = T_{c1}-T_{co} \pm \varepsilon$ (K)
0.50	0.0280	−3.6±0.1	−2.6±0.1
0.56	0.0457	−6.0±0.1	−5.0±0.1
0.63	0.0485	−6.5±0.1	−5.4±0.1
1.94	0.1191	−13.4±0.3	−12.0±0.3
3.50	0.1850	−17.4±0.5	−15.4±0.5
3.60	0.2050	−18.2±0.6	−16.2±0.6

A. Experimental details

Single crystals of Cu^{2+}:ZTFH were grown by slow evaporation of an aqueous solution obtained by dissolving $ZnCO_3$ in 40% H_2TiF_6 with $CuCO_3$ added to obtain various Cu^{2+} concentrations. Recrystallization was carried out in all crystals to reduce the Mn^{2+} impurity concentration beyond the EPR detection limit. To grow single crystal of Ni^{2+}:ZTFH, $NiCO_3$ was used instead of $CuCO_3$. The crystals grow with the (110) type planes surrounding the [111] axis, which is along the length of the crystal. Only good single crystals devoid of any twinning and with uniform coloration (bluish green for Cu^{2+} and greenish for Ni^{2+}) were chosen for EPR studies of T_{c1} of these crystals. The impurity concentration, c (wt %) was analyzed by Galbraith Laboratories, Tennessee, USA. EPR Q-band spectra were performed in the (110) direction of the crystal with the magnetic field direction along the $g_{\max}$ (Ref. 11) [this direction is close to the $g_{\|}$ direction or (100) direction of the Cu^{2+} ion and corresponds to the maximum g value in the (110) plane]. The accuracy of determination of the onset of the phase transition is the highest in this direction because of the appearance of as many as six lines with the largest magnetic field separations. Above T_{c1}, the EPR spectrum consists of an isotropic line only. It is not possible to determine the phase transition along the (111) direction because all EPR lines remain overlapped even after the phase transition, except for the appearance of four copper hyperfine lines at around 120 K. The EPR spectrometer used was a Q-band (33–35 GHz) reflectance spectrometer built in Physics Department UTA, Texas. Temperatures were varied by manual control with an approximately uniform cooing and heating rate that can be varied between 1 °C/min to 1 °C/120 min. The sample could be maintained at any temperature above 77 K to within ±0.1 °C for 30 min. The samples' temperature was measured by both E- and T-type thermocouples with digital readout, calibrated at the standard temperatures of liquid N_2, solid CO_2, liquid N_2 slush with toluene and a mixture of isopropane and solid CO_2. For measurement of T_{c1}, each sample was kept in vacuum during the entire experiment to prevent moisture accumulation on the sample.

B. Precise determination of transition temperature

1. Measurement of T_{c1} for Ni^{2+}:ZTFH

The sample was cooled at a rate of 3 °C h^{-1} down to 1 °C above the phase transition and then cooled at the rate of 0.5 °C h^{-1}. For recording T_{c1} during warming, the sample was cooled well below T_{c1} first and then warmed at a rate of 3 °C h^{-1} up to 1 °C below T_{c1} and then warmed at a rate of 0.5 °C h^{-1}. The transition temperature T_{c1} for Ni^{2+}:ZTFH was measured by orienting the [111] axis of the crystal parallel to the magnetic field and observing the changes in the EPR transitions between the spin states $M_s=|+1\rangle$ and $M_s=|0\rangle$ of the ground orbital singlet state. Methods of determination of T_{c1} with Ni^{2+} impurity probe can be obtained from Refs. 18–21. At T_{c1} the changes are quite sharp. Table I shows changes in T_{c1} for Ni^{2+}:ZTFH with varying Ni^{2+} concentrations. Note that our detailed studies of the phase transitions in doped crystals of ZTFH have not revealed any second transition at T_{c1} (217 K) in pure ZTFH as observed by Choudhury *et al.*[4–7] Therefore, in the subsequent studies we focus only on T_{c1}.

2. Measurement of T_{c1} for Cu^{2+}:ZTFH

The transition temperature was obtained by recording the variation in the intensity of the isotropic EPR signal (I_s) as the sample was cooled at a uniform rate of 3 °C h^{-1} down to about 1 °C above the phase transition. The sample is then cooled at a rate of 0.5 and 1.5 °C h^{-1} for Cu^{2+} concentration up to and above 1.81 wt %, respectively. The spectra were then run with a magnetic field sweep time of 5 min. If all EPR instrumental parameters are kept constant then the EPR signal intensity, I_s increases with decreasing temperature under normal circumstances (i.e., no phase transition). In the vicinity of phase transition, however, the intensity decreases on cooling around T_{c1} (Fig. 1). T_{c1} during cooling ($T_{c1}\downarrow$) can be detected by the appearance of the high-field lines or by noticeable reduction (with all the spectrometer parameters such as frequency, gain, time constant, sweep time, field sweep range, etc. remaining constant) of I_s as high as 60% in crystal with low impurity concentration with a temperature variation of ~0.1 °C (Fig. 1). For low Cu^{2+} concentration (0.043 wt %), it can be seen (Fig. 1) that at 170.6 K there is a noticeable change in I_s from that at 170.7 K. This is accompanied by the appearance of high-field signals, which are prominent at 170.5 K and below. So, $T_{c1}\downarrow$ for this Cu^{2+} concentration could be determined as 170.6±0.2 K (0.05 K is the error in the temperature recording). The high and low-temperature phases coexist over a finite temperature range, ΔT_c, which increases with impurity concentration. Figure 2

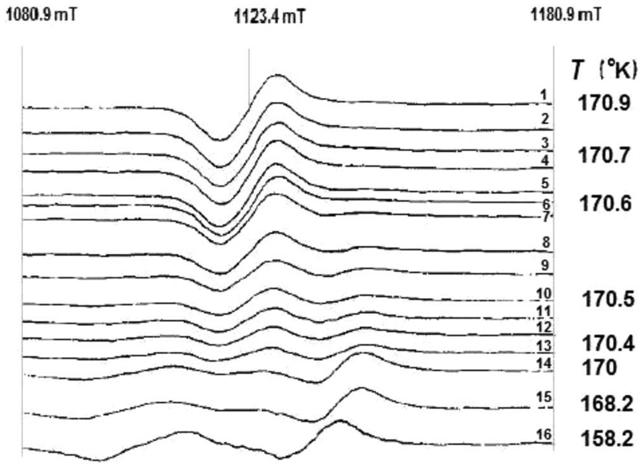

FIG. 1. EPR spectra for low Cu^{2+} (0.043 wt %) in $ZnTiF_6 \cdot 6H_2O$ single crystal in the immediate vicinity of phase transition temperature. Temperatures (T) of curves 1 and 2, T(1,2): 170.9 K; T(3,4): 170.7 K; T(5,6,7): 170.6 K; T(8,9,10): 170.5 K; T(11,12,13): 170.4 K; T(14): 170 K; T(15): 168.2 K; T(16): 158.2 K.

represents a similar recording for a higher Cu^{2+} ion concentration (3.7 wt %), where unlike the sharp transition observed for low Cu^{2+} concentration (Fig. 1), the transition is gradual with respect to the change of temperature about T_{c1} in contrast to the sharp transition observed for low Cu^{2+} concentration (Fig. 1). For high impurity concentration T_{c1} is measured by noting the temperature at which a noticeable decrease in the EPR signal intensity is first observed upon cooling. It is seen from Fig. 2 that T_{c1} is significantly lower from that in Fig. 1.

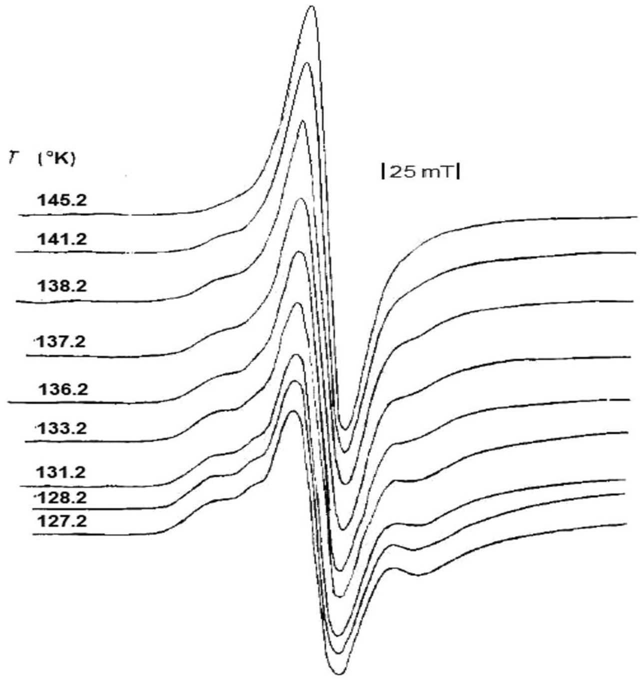

FIG. 2. The EPR spectrum recorded for Cu^{2+} concentration of 3.7 wt % in ZTFH in the same orientation as in Fig. 1

During warming from low-temperature phase, the transition is noticed by changes taking place in the reverse order. However, for all the samples investigated with different Cu^{2+} concentrations (Table II), $T_{c1}\uparrow$ during warming from the low-temperature phase is found to be slightly higher than the transition temperature $T_{c1}\downarrow$ during cooling from the trigonal phase. This hysteresis is due to the coexistence of two phases as mentioned earlier. Relaxation between the two phases can be responsible for the observed differences in the $T_{c1}\downarrow$ and $T_{c1}\uparrow$ (Table II) for various Cu^{2+} concentrations in ZTFH. It is seen from Table II that T_{c1} measured by this method decreases with Cu^{2+} impurity concentration and is independent of the orientation of the magnetic field. This shows that the mechanism driving the transition has isotropic nature. In Table II footnote, we mention the maximum possible error ε in the determination of T_{c1}. ε depends on the sharpness of the transition with respect to change in T around T_{c1}, despite the fact the accuracy of temperature measurement is fairly constant (± 0.05 K) over the temperature range investigated. For example, for the lowest Cu^{2+} concentration (0.043%), the transition is quite sharp and the error ε is quite low (± 0.2 K) compared to that of 3.7% Cu^{2+} where the transition is not sharp.

II. THEORETICAL EXPLANATION OF VARIATIONS OF PHASE TRANSITION WITH IMPURITY

There has not been enough data or satisfactory theory on the study of modification of phase transition of host lattice with impurity. For a theory that explains the observed changes in T_c (i.e., $\Delta T_c = T_c - T_{co}$) with impurity content to be reasonable, it must involve the atomic fraction x of the impurity.[22] In principle, ΔT_c can be explained either by: (i) thermodynamic approach or (ii) soft-mode concept. In the thermodynamic approach, it is envisaged that the impurity changes the free energy of the system, whereas in the soft-mode concept it is assumed that the impurity brings about a change in the soft-mode frequency of the host lattice.[16,17] Soft-mode approach is quite advanced and requires application of group theory and experimental identification of the particular soft mode responsible for the phase transition. It also requires the coupling of the soft mode with the Jahn-Teller modes in case of Cu^{2+} doped ZTFH crystals. In this study we adopt the thermodynamic approach and develop the necessary equations for Ni^{2+}:ZTFH crystals first and then extend the ideas to Cu^{2+}:ZTFH crystals. It is to be noted that Ni^{2+}:ZTFH is much simpler to deal with than Cu^{2+}:ZTFH where the mechanism of contributions of the Jahn-Teller effect to ΔT_{c1} is yet unclear. The molecular mass of the doped crystal $Zn_{1-x}Ni_xTiF_6 \cdot 6H_2O$ is given by $M_x = (1-x)M_{Zn} + xM_{Ni} + M_{Ti} + 6M_F + 6M_{H_2O}$, where M is the atomic mass of the element or compound, whose symbol is denoted as subscript. Substituting the atomic masses of the elements gives $M_x = 335.3 - 6.7x$. Therefore, the percentage weight (c) of the Ni^{2+} ion impurity in Ni^{2+}:ZTFH.

$$c = \frac{58.7x}{335.3 - 6.7x} \times 100\%. \tag{1}$$

This yields

TABLE II. Observed changes in the phase transition temperature ($\Delta T_{c1}=T_{c1}-T_{co}$) (°C) in $\mathrm{Cu}^{2+}:\mathrm{ZnTiF}_6\cdot 6\mathrm{H}_2\mathrm{O}$ with varying Cu^{2+} concentration; T_{co} for pure lattice=182 K=−91.2 °C.

Concentration[a], c wt % ±0.01	Atomic fraction, x	On cooling $\Delta T_{c1}\downarrow = T_{c1}-T_{co}\pm\varepsilon$ (K)	On warming $\Delta T_{c1}\downarrow = T_{c1}-T_{co}\pm\varepsilon$ (K)
0.043	0.0053	-11.4 ± 0.1	−9.8
0.38	0.0195	-14.1 ± 0.2	−11.0
0.50	0.0227	-15.4 ± 0.2	−12.9
0.63	0.0317	-16.0 ± 0.3	−14.1
0.69	0.0370	-17.3 ± 0.4	−15.4
0.94	0.0495	-19.1 ± 0.5	−17.3
1.06	0.0528	-20.4 ± 0.6	−19.9
1.44	0.0723	-26.3 ± 1.0	−24.4
1.81	0.0950	-27.9 ± 1.3	−26.3
3.70	0.1952	-41.0 ± 2.0	−38.8
8.94	0.4710	-71.0 ± 5.0	

[a] The concentration is determined spectroscopically by Galbraith Analytical Laboratories Inc., Tennessee, USA. For $0<c<1.06$, $0.2<\varepsilon<1$; $1.96<c<1.81$, $1<\varepsilon<2$; $c=3.7$, $2<\varepsilon<3$; $c=8.94$, $5<\varepsilon<6$.

$$x=\frac{335.3c}{5870+6.7c}. \tag{2}$$

Similarly, for Cu^{2+}:ZTFH we obtain

$$c=\frac{63.5x}{335.3-1.9x}\times 100\%, \tag{3}$$

$$\text{and}\quad x=\frac{335.3c}{6350+1.9c}. \tag{4}$$

A. Host lattice exhibiting first-order transition

To our knowledge there is no theory connecting change in-phase transition temperature with impurity atomic fraction, x in a host lattice. We make an attempt here to derive this relation from the free-energy stand point. The phenomenological theories of second-order phase transition (2nd PT) are based on symmetry criteria.[23] In these theories and those for ferroelectrics the free energy is expanded in powers of polarization coefficients, which in general are functions of temperature and pressure or stress.[24] The polarization can be considered as an order parameter of the crystal. Following Landau[23,25] the free energy f can be expanded in a power series of order parameter η in the second phase,

$$f=f_o+A\eta^2+B\eta^4+C\eta^6+\ \dots, \tag{5}$$

f_o refers to the free energy of the first phase. In case of second-order transition the first-order derivative of f with respect to η (order parameter) changes continuously according to the relation,

$$\frac{\partial f}{\partial\eta}=0,\quad \frac{\partial^2 f}{\partial\eta^2}>0. \tag{6}$$

The second-order phase transition temperature T_o is a temperature where the two phases are at equilibrium. In the case of first-order transition where $\partial f/\partial\eta$ changes discontinuously; Landau's criteria demands $f(\eta)=f_o$. Using these conditions, it can be easily shown that [by retaining up to sixth power of η in expansion of f Eq. (5)] the temperature of the first-order transition temperature, T_c (corresponding to low impurity concentration in ZTFH crystals) can be given by

$$T=T_o+\frac{B^2}{2KC}, \tag{7}$$

where the order parameter changes discontinuously from zero to a value,

$$\eta=\left(-\frac{B}{2C}\right)^{1/2}, \tag{8}$$

and K is the Landau mean-field constant in $A=K(T-T_o)$. Equation (7) gives the relation between the first-order transition temperature, T_c and the second-order transition temperature T_o.

Further development of the theory is based on the following assumptions. First, the spring constant of the lattice atoms remains unchanged with introduction of impurity at low concentration. This is reasonable especially if the impurity substitutes the host lattice atom of the same valency. Both Cu^{2+} and Ni^{2+} ions separately doped in ZTFH crystal are confirmed by EPR (Refs. 11 and 27) to replace Zn^{2+} ion. We denote the term B in Eq. (7) for pure $\mathrm{ZnTiF}_6\cdot 6\mathrm{H}_2\mathrm{O}$ as B_o and the corresponding T_c as T_{co} i.e., $T_{co}=T_o+\frac{B_o^2}{2KC}$ for $x=0$.

The impurity Ni^{2+} in $\mathrm{Zn}_{1-x}\mathrm{Ni}_x\mathrm{TiF}_6\cdot 6\mathrm{H}_2\mathrm{O}$ causes perturbation in the anharmonicity of the lattice. The anharmonic term B_o is particularly perturbed by the impurity, changing to

$$B=B_o\pm\Delta B. \tag{9}$$

Then from Eq. (7) we obtain several alternative equations,

$$T_c=T_o+\frac{(B_o+\Delta B)^2}{2KC}=T_{co}+\alpha\Delta B+\sigma^2\Delta B^2, \tag{10}$$

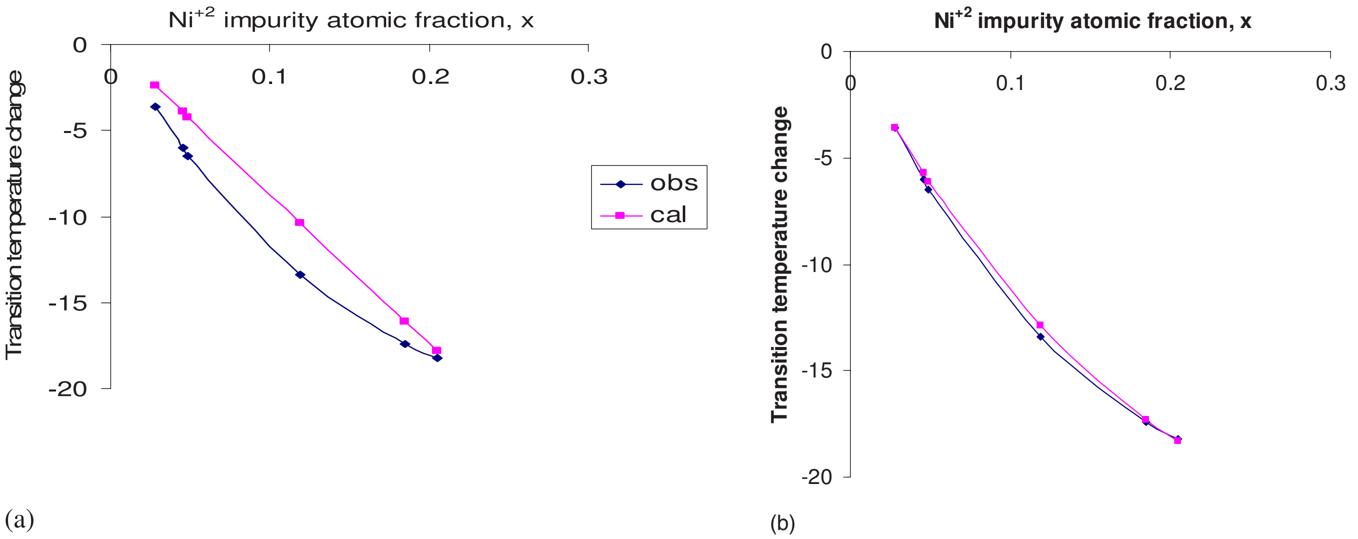

FIG. 3. (Color online) First (a) and second (b) approximation fitting of ΔT_c (obs) and ΔT_c (cal) versus atomic fraction, x for Ni^{2+} in ZTFH.

$$\text{or}\quad \Delta T_c = T_c - T_{co} = \alpha\Delta B + \sigma^2\Delta B^2, \tag{11}$$

where the phase transition temperature of the pure ZTFH crystal $T_{co}=T_o+\frac{B_o^2}{2KC}$, $\alpha=\frac{B_0}{KC}$, $\sigma^2=\frac{1}{KC}$ and subscript "0" refers to zero impurity in crystal. Thus, as a first-order approximation for low x.

$$T_c = T_{co} + \alpha\Delta B. \tag{12}$$

Introduction of Ni^{2+} impurity in $ZnTiF_6 \cdot 6H_2O$ causes slight perturbation in the vibration frequency of the lattice, thus changing the free energy of the system. Another contribution can be from the change in the elastic energy of the lattice as a result of change of elastic constants due to the impurity. When Ni^{2+} substitutes Zn^{2+}, the vibrational frequency that is affected is due to the $[Zn, 6H_2O]$ octahedral chromophore. With impurity Ni^{2+} in $ZnTiF_6 \cdot 6H_2O$, change in ΔB is given by

$$\Delta B = \beta\left[\frac{1}{M(Zn,6H_2O)} - \frac{1}{(1-x)M_{Zn} + xM_{Ni} + 6H_2O}\right]. \tag{13a}$$

Substituting the values (see Sec. II) we obtain

$$\Delta B = \gamma\frac{6.7x}{173.4 - 6.7x}, \quad \text{where} \quad \gamma = \frac{-\beta}{173.4}. \tag{13b}$$

Equation (13a) and (13b) satisfies the condition that $\Delta B=0$ for $x=0$. Substituting Eq. (13a) and (13b) in Eq. (11) yields

$$\Delta T_c = a\left(\frac{6.7x}{173.4 - 6.7x}\right) + b\left(\frac{6.7x}{173.4 - 6.7x}\right)^2, \tag{14}$$

where $a=\alpha\gamma$ and $b=a^2\gamma^2$ are constants. Equation (14) describes the variation in T_c with the atomic fraction x of Ni^{2+} impurity in the host crystal of $ZnTiF_6 \cdot 6H_2O$. We expect the constants a and b to be characteristics of the host crystal.

B. Fitting of the experimental data with Ni^{2+} in ZTFH crystals

First, we do the least square fit of the observed ΔT_c (obs) and calculated ΔT_{c1} (cal*) listed in Table I for Ni^{2+} [see Fig. 3(a)] neglecting the second term in Eq. (14). This yields the constants $a=-2034$ as expected negative because ΔT_c is negative (i.e., T_c decreases with x). Next, we do similar fitting using the two constants "a" and "b" in Eq. (14) and obtain $a=-3517$ and $b=155078$ [see Fig. 3(b)] using ΔT_c (cal**) listed in Table III. Figure 3 indicates that the observed change in the transition temperature of $Zn_{1-x}Ni_xTiF_6 \cdot 6H_2O$ single crystal as a function of x may be explained from the thermodynamic principle of phase transition and Landau's concept of dependence of free energy of the lattice on the order parameter and assumption of the change in free-energy term with x.

Using Eq. (11), we see excellent fit between the experimental and observed values of ΔT_c as a function of x (see Fig. 3(b)). This proves the validity of the assumptions made in deriving the theoretical expression for ΔT_c [Eq. (11)] as a function of x in $Zn_{1-x}Ni_xTiF_6 \cdot 6H_2O$ crystals.

C. Host lattice with JT impurity exhibiting phase transition

We want to extend the ideas for Ni^{2+}:ZTFH to explain the ΔT_c for Cu^{2+} impurity in ZTFH crystal. Replacing M_{Ni} by M_{Cu} in Eq. (13a) we get for Cu^{2+}:ZTFH

TABLE III. Observed and calculated ΔT_c for various atomic fraction x of Ni^{2+} in $Zn_{1-x}Ni_xTiF_6 \cdot 6H_2O$ single crystals.

x	ΔT_c (obs)	ΔT_c (cal*)	ΔT_c (cal**)
0.0.0280	−3.6	−2.4	−3.6
0.0457	−6.0	−3.9	−5.7
0.0485	−6.5	−4.2	−6.1
0.1191	−13.4	−10.4	−12.9
0.1850	−17.4	−16.1	−17.3
0.2048	−18.2	−17.8	−18.3

$$\Delta B = \beta\left[\frac{1}{173.4} - \frac{1}{173.4 - 1.9x}\right] = \frac{\gamma 1.9x}{173.4 - 1.9x}, \quad (15)$$

where γ is the same as in Eq. (13b). Using Eq. (11), now for Cu^{2+}:ZTFH,

$$\Delta T_c = a\left(\frac{1.9x}{173.4 - 1.9x}\right) + b\left(\frac{1.9x}{173.4 - 1.9x}\right)^2, \quad (16)$$

where a and b are the same as those obtained for Ni^{2+}:ZTFH, i.e., $a = -3517$ and $b = 155078$. Using Eq. (16) we could not obtain a fit that would come even close to the observed variation of ΔT_c with x for Cu^{2+}:ZTFH crystal.

It has been established earlier by De[11] that Cu^{2+} impurity in ZTFH crystal exhibits Jahn-Teller effect. Comparing Tables I and II we see a significantly enhanced reduction in T_c for Cu^{2+} impurity compared with Ni^{2+} impurity of similar concentration. The differences in ionic masses and radii of the impurity from that of Zn^{2+} ion are higher for Ni^{2+} than of Cu^{2+}. So the observed enhanced reduction in T_{c1} for Cu^{2+} may be attributed to the coupling of the Jahn-Teller modes with the soft modes of the host lattice. Actual evaluation of this coupling and its effect on the modification of phase transition is beyond the scope of this paper. Jahn-Teller effect involves coupling of the ground degenerate orbital states of the JT ion with the vibrational modes of the nearest-neighbor ligand cluster of similar symmetries. The resulting modes are as vibronic modes. When the said coupling is extended to the entire phonon modes of the host lattice the effect is known as multimode JT effect.[28–30] In this situation the properties of the JT impurity become slightly modified compared to that of single mode JT effect. However, the effect of this is expected to be ordinarily small because the induced JT distortion extends only over a few lattice distances. But in a situation where the coupling involves the soft-mode of a structural phase transition of the host crystal, the range of the distortion becomes appreciable and increases as the critical temperature is approached, and an initially weak JT effect changes into a strong JT effect close to the transition temperature.[30]

On the other hand, the properties of the structural transition in the host lattices also become considerably modified due to the coupling of JT effect to the soft mode of the transition. In most cases such modifications manifest in the form of changes in the frequencies of the soft mode or a shift in the transition temperature.[28–30] Now in the present investigation, we have seen that the JT ion Cu^{2+} induces significantly greater changes in T_c compared to non-JT ion Ni^{2+} of similar atomic fraction. In the light of the above discussion we want to examine the validity of the above theory with an introduction of a modification factor δ in the expression for ΔB as given below [Eq. (17)] for $Zn_{1-x}Cu_xTiF_6 \cdot 6H_2O$ crystals in order to account for the phase transition temperature T_c, significantly modified by Jahn-Teller impurity,

$$\Delta B = \beta\left[\frac{1}{173.4} - \frac{\delta}{173.4 - 1.9x}\right] = -\gamma\left[\frac{173.4(1-\delta) - 1.9x}{173.4 - 1.9x}\right]. \quad (17)$$

TABLE IV. Observed and calculated changes to the phase transition temperature ΔT_c for various values of atomic fraction of Cu^{2+} ion impurity x in $Zn_{1-x}Cu_xTiF_6 \cdot 6H_2O$ single crystals.

Atomic fraction, x	Enhancement factor, δ	ΔT_c(obs) $\pm \varepsilon$ (K)[b]	ΔT_c(cal) ± 0.1 K
0.0053	1.00375	−11.4	−11.4
0.0195	1.00500	−14.1	−14.3
0.0227	1.00570	−15.4	−15.4
0.0317	1.00600	−16.0	−16.1
0.0370	1.00700	−17.3	−17.6
0.0495	1.00840	−19.1	−19.0
0.0528	1.01000	−20.4	−19.9
0.0723	[a]	−26.3	[a]
0.0950	[a]	−27.9	[a]
0.1952	[a]	−41.0	[a]
0.4710	[a]	−71.0	[a]

[a] Theory could not explain these concentrations for reasons given in the text.

[b] For errors in ΔT_c (obs) see Table II.

Substituting Eq. (17) in Eq. (11) gives

$$\Delta T_c = -\alpha\gamma\left[\frac{173.4(1-\delta) - 1.9x}{173.4 - 1.9x}\right] + \alpha^2\gamma^2\left[\frac{173.4(1-\delta) - 1.9x}{173.4 - 1.9x}\right]^2 = a'L + bL^2 \quad (18)$$

where $L = [173.4(1-\delta) - 1.9x]/(173.4 - 1.9x)$, $a' = -a = 3517$, $b = 155078$ same as those for Ni^{2+} in ZTFH. By allowing for a small variation in δ in Eq. (18) we obtain the fitting as given in Table IV.

III. DISCUSSIONS

In this study we have found through EPR experiments that phase transition temperature T_{c1} of single crystals of $ZnTiF_6 \cdot 6H_2O$ (ZTFH) decreases with an increase in the impurity concentration of Ni^{2+} or Cu^{2+}.[11] We have observed that the decrease in T_{c1} due to JT impurity (Cu^{2+}) is much greater than that due to non-JT impurity (Ni^{2+}). Note that during our investigation we did not observe the second transition in the doped ZTFH crystals as reported by Das *et al.*[8] to occur at 217 K in pure crystal. Therefore, in the theoretical study (see Sec. III) we did not consider the influence of the second transition on T_{c1}.

In this study, attempts have also been made to theoretically explain the experimental observation of the changes of T_{c1} in $ZnTiF_6 \cdot 6H_2O$. For Ni^{2+} impurity, the change in T_{c1} with impurity atomic fraction, x has been explained from the thermodynamic free-energy stand point. The Ni^{2+} impurity ion is assumed to cause a change in the vibrational frequency of the $[Zn, 6H_2O]$ chromophore, which in turn changes the free energy of the system. Theoretical equations relating change in the transition temperature with atomic fraction of the impurity (x) have been derived. Excellent fit between the observed and theoretically computed changes of (ΔT_{c1}) versus x for Ni^{2+} impurity in $ZnTiF_6 \cdot 6H_2O$ has been obtained for $a=-3517$ and $b=155078$. For low values of x, the elastic constants of ZTFH may be assumed to remain unchanged. The values of a and b may then be assumed to be characteristics of the ZTFH host lattice. Using the same values of a and b for ZTFH we tried to theoretically fit the observed change of T_{c1} for JT Cu^{2+} ion in $ZnTiF_6 \cdot 6H_2O$ using the concept of an enhancement factor δ in Eq. (18). The fit is excellent when δ is allowed to vary slightly with x up to $x=0.0528$. Even though δ is found to differ from unity by only a small amount (Table IV) it has significance in explaining quantitatively the observed changes in T_{c1} for x up to $x=0.0528$ for Cu^{2+}:ZTFH crystal. The theory practically failed for higher concentrations, $x > 0.0528$ (Table IV). One of the reasons could be that for low concentration the observed phase transition is of the first order as marked by an abrupt decrease in the isotropic EPR signal intensity and appearances of new lines (which are anisotropic at and below transition temperature).[11,26] For higher Cu^{2+} ion concentrations the observed transition is continuous and closer to second-order transitions. It is possible that for higher Cu^{2+} concentrations, the cooperative Jahn-Teller effect sets in. Then explanation of the observed modification of phase transition for $x(Cu^{2+}) > 0.0528$ would require a new theory. It is recommended for further theoretical studies as it may reveal new physics. Such further studies would involve the interaction of Jahn-Teller modes as a function of $x(Cu^{2+})$ with the soft mode of the host lattice to arrive at an expression of ΔT_{c1} for higher atomic fraction x. The soft mode may be identified with the rotation of the fluorine octahedral, which in pure lattice freezes at $T_{c1}=182$ K. Any new theory should also take into account the lowering of one of the three Jahn-Teller potential wells[12] with respect to the other two at temperature, T.[11,15,31] Such lowering is not seen in Jahn-Teller systems such as Cu^{2+} doped in $ZnSiF_6 \cdot 6H_2O$ crystals, the system where Jahn-Teller effect was first experimentally confirmed[32] as well as in other systems such as: $Cu^{2+}:La_2Mg_3(NO)_{12} \cdot 24D_2O$, $(BrO_3)6H_2O$ (Refs. 33 and 34) single crystals. All these systems, however, do not exhibit structural phase transition in contrast to the present system studied. In the derivation of our theory we have not considered the influence of the ionic radii of the impurity ions on the strain of the lattice, which may also results in modification of T_c. In our present systems, however, this may not be a major problem, since the ionic radii of the two impurities are not much different. The detailed investigation on the exact influence of the ionic radii of the impurity ions in modification of phase transition temperature is underway and will be reported later.

IV. CONCLUSION

In this study, we investigate using EPR experiments, the transition temperature T_{c1} of ZTFH crystals doped with Ni^{2+} or Cu^{2+} impurity. We find T_{c1} decreases significantly with increasing Ni^{2+} or Cu^{2+} concentration, the decrease being much greater for Jahn-Teller Cu^{2+} impurity than for non Jahn-Teller Ni^{2+} ion. Attempts have been made to theoretically explain the experimental observations of the change in phase transition temperature T_{c1} with Ni^{2+} or Cu^{2+} atomic fraction, (x) in $Zn_{1-x}M_xTiF_6 \cdot 6H_2O$ crystals (M=impurity ion) from thermodynamic free-energy principle. For Ni^{2+} impurity, the observed change in T_{c1} as a function of x has been quantitatively explained very well by our theory. Using the same values of a and b (assumed to be characteristic of the host lattice ZTFH) derived from the fit of the data of Ni^{2+} impurity, we tried to theoretically fit the observed changes for $Cu^{2+}:ZnTiF_6 \cdot 6H_2O$ using the concept of an enhancement factor δ. The fit was found to be good only when δ was allowed to vary slightly above unity with x up to $x=0.0528$. The fit was found to be poor for higher concentrations, $x > 0.0528$. For low concentration the observed phase transition[35] is of first order as indicated by abrupt decrease in the isotropic EPR signal intensity and appearances of new lines (which are anisotropic at transition temperature). This was successfully explained by our theory for first-order transition. For higher Cu^{2+} ion concentration the observed transition is continuous and closer to second-order transition. One of the reasons our theory practically failed for higher Cu^{2+} ion concentrations could be that it is possible cooperative Jahn-Teller effect sets in, thus requiring another explanation of the observed modification of phase transition temperature with higher Cu^{2+} ion concentrations.

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*Author to whom correspondence should be addressed. Present address: Department of Physics, Federal University of Technology, P. M. B. 2076 Yola, Nigeria. dipak61@yahoo.com

†bejakwa@yahoo.com

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