

Full Length Research Paper

Dependence of temperature variation of the Jahn-Teller potential well splitting and phase transition temperature in $\text{Cu}_x\text{Zn}_{1-x}\text{TiF}_6 \cdot 6\text{H}_2\text{O}$ crystals on Cu^{2+} ion concentration, x

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The energy E_o by which one of the three Jahn-Teller potential wells becomes lower than the other two in $\text{Cu}^{2+}:\text{ZnTiF}_6 \cdot 6\text{H}_2\text{O}$ single crystal at phase transition temperature, T_{cl} are determined at temperatures below T_{cl} for different Cu^{2+} concentrations from the electron paramagnetic resonance (EPR) spectra. As the sample is cooled, it is found that for high Cu^{2+} concentration, E_o increases below T_{cl} at a rate much slower than that for low concentration and over a much broader temperature range. With the increase of Cu^{2+} concentration, T_{cl} is found to decrease significantly. These findings appear to have a bearing on the monoclinic distortion that proceeds in this system below T_{cl} . Qualitative explanation of the decrease of T_{cl} with Cu^{2+} impurity concentration is presented. E_o is negligibly small for Cu^{2+} concentrations above certain limits means that the barrier height is also vanishing for such Cu^{2+} concentrations that is, phase transition of host lattice ceases. This is likely the reason for non-existence of phase transition in some compounds like $\text{CuTiF}_6 \cdot 6\text{H}_2\text{O}$ and $\text{ZnSiF}_6 \cdot 6\text{H}_2\text{O}$ belonging to the same class with $\text{ZnTiF}_6 \cdot 6\text{H}_2\text{O}$.

Key words: $\text{ZnTiF}_6 \cdot 6\text{H}_2\text{O}$, Cu^{2+} , Jahn-Teller potential.

INTRODUCTION

The discovery of electron paramagnetic resonance (EPR) can be traced to the experimental work on resonance in salts of the iron group ions carried out by Zavoisky at Kazan in Russia (Zavoisky, 1945). Today, EPR has applications in physical sciences for studying phase transitions and other solid interactions (Maulin et al., 2001; Shiyamala et al., 2002; Malkova et al., 2003; Dunbar et al., 2003; Klupp et al., 2006), biological systems—mostly irradiated samples (Stosser et al., 2003) and geosciences for dating and radiation dosimetry (Sutter et al., 2002). Recently, a general review on EPR studies of phase transitions and Jahn-Teller (JT) effect in

paramagnetic systems was made (Yerima, 2005). Yerima and De (2004) carried out EPR studies on deviation from mean field theory of phase transition in $\text{CaCd}(\text{CH}_3\text{OO})_4 \cdot 6\text{H}_2\text{O}$ single crystals for different Cu^{2+} ion concentrations. In this introductory part, a general review of previous works on modification of phase transition and other solid interactions due to impurities in host lattice (ZTFH) of interest is discussed as follows:

Similar to certain copper-doped compounds of the class $\text{ABF}_6 \cdot 6\text{H}_2\text{O}$ (A = a divalent metal, B = a tetravalent metal, Ti, Si, Ge, etc.), the crystal zinc fluotitanate hexahydrate, $\text{ZnTiF}_6 \cdot 6\text{H}_2\text{O}$ (ZTFH), displays a Jahn-Teller effect characterized by a slow gradual decrease in the anisotropy of the electron paramagnetic resonance (EPR) spectrum as the temperature is increased above 4 K. The crystal structure of this class consists of nearly regular

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$A(H_2O)_6$ and BF_6 octahedra packed in a trigonally distorted structure similar to that of CsCl. Many compounds of the above series exhibit first-order structural phase transitions in the temperature range 130 - 300 K, from the high-temperature trigonal phase (R m) to the low temperature monoclinic phase (P21/C) (Wyckoff, 1965; Syoyama and Osaki, 1972).

^{19}F NMR studies (Afanasyev et al., 1979) reveal a first-order phase transition at 182 K (T_{cl}) when the rotation of the fluorine octahedra freezes and the single ^{19}F line splits into two, indicating the loss of a chemical equivalence between the fluorine atoms, following a tetragonal distortion of the $[TiF_6]^{2-}$ octahedra. However, at T_{cl} , no appreciable change in the 1H resonance was observed and accordingly they postulated that a change in the $[Zn(6H_2O)]^{2+}$ symmetry caused a sudden transition in $ZnTiF_6 \cdot 6H_2O$. A weak transition of a continuous nature at 217 K (T_{c2}) was indicated through the combined infrared, Raman, dielectric and thermal expansion measurements of Choudhury et al. (1981; 1983; 1986a/b). They concluded that the weak transition at 217 K is associated with the tilt of the $[M^{2+}, H_2O]$ octahedra. While an abrupt contraction in the c direction and an 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. (1985) theoretically investigated the various coupling between the vibrational and rotational modes of $[TiF_6]^{2-}$ and $[M^{2+}, H_2O]$ octahedra. Bose et al.'s 2H NMR studies (Bose et al., 1983; 1987) in $ZnTiF_6 \cdot 6H_2O$ and deuterated crystals of similar structure confirmed two phase transitions in these materials, with R m symmetry above the upper transition, P21/C symmetry below the lower transition, and an undetermined unimolecular intermediate phase.

Cu^{2+} ion in ZTFH has an orbitally degenerate $2E$ ground state. De et al (1984) detailed EPR studies on Cu^{2+} doped ZTFH revealed that the Cu^{2+} ions in this system exhibit a strong Jahn-Teller effect as expected (O'Brien and Chancey, 1993). With a low Cu^{2+} concentration of 0.043% weight (% wt), the transition temperature, T_{cl} was lowered by 110C from that (182 K) of pure ZTFH; and further lowering in T_{cl} occurred when the crystal was powdered (De, 1986). Rubins et al. (1989) studied the trigonal to monoclinic phase transition in ZTFH as a function of Mn^{2+} concentration. In contrast to the said lowering of T_{cl} , they found that Mn^{2+} ion in this crystal increases the T_{cl} , in common with other measurements in $ZnGeF_6 \cdot 6H_2O$ Ziatdinov et al., 1983).

The JT stabilization energy $E_{JT} = 1000cm^{-1}$ has been determined by De (1986) from a fit of the EPR linewidth, which varies exponentially with temperature, to an Orbach relaxation mechanism. A study (De et al., 1984) of the gradual variation of the spin Hamiltonian para-

eters $g_{||}$, g_{\perp} , $A_{||}$, A_{\perp} down to 4.2 K, has shown that one of the three JT potential wells (O'Brien and Chancey, 1993) is lower than the other two, by an energy, E_0 , of about $140 cm^{-1}$. The lowering of one of the Jahn-Teller potential wells by $150 cm^{-1}$ relative to the other two was also postulated by Ziatdinov et al. (1983) in the case of Cu^{2+} in $ZnTiF_6 \cdot 6H_2O$. Later, Rubins and Drumheller (1987) carried out a further study of the EPR spectrum of Cu^{2+} in $ZnTiF_6 \cdot 6H_2O$ between 4 K and 160 K and concluded that for low Cu^{2+} concentration, E_0 has small temperature dependence below T_{cl} .

It is to be noted that such lowering of potential well does not occur in $Cu^{2+} \cdot ZnSiF_6 \cdot 6H_2O$ crystals, the system where Jahn-Teller effect was first experimentally confirmed (Pilbrow, 1990), as well as in other systems which exhibit no structural phase transition such as: $Cu^{2+} \cdot La_2Mg_3(NO_3)_{12}24D_2O$, $Cu^{2+} \cdot (BrO_3)_26H_2O$ (Breen et al., 1969), etc. E_0 in $Cu^{2+} \cdot ZnTiF_6 \cdot H_2O$, or $Cu^{2+} \cdot ZnGeF_6 \cdot 6H_2O$ can be taken as a measure of the monoclinic distortion below T_{cl} in these crystals. However, previous studies have not clearly focused on the impurity concentration dependence of the behavior of E_0 with temperature as the sample is cooled well below T_{cl} . In this study we have tried to address this issue together with the nature of dependence of phase transition temperature (T_{c1}) on Cu^{2+} ion impurity concentration in ZTFH.

EXPERIMENTAL

Single crystals of ZTFH were grown by slow evaporation of an aqueous solution of $ZnTiF_6$ obtained by dissolving $ZnCO_3$ in 40% H_2TiF_6 . $CuCO_3$ was added to grow doped crystal of various Cu^{2+} concentrations. Re-crystallization was carried out to reduce the Mn^{2+} impurity concentration beyond the EPR detection limit in all of the crystals investigated with varying Cu^{2+} ion concentrations. Only good single crystals devoid of any twinning and with uniform coloration due to the Cu impurity (bluish green for Cu) were chosen for the experiments. The same crystal samples (for which T_{cl} s were obtained from EPR experiments) were analyzed by Galbraith Laboratories, Tennessee, USA using standard spectroscopic technique for estimation of the impurity concentration. The Cu^{2+} concentrations in the three different samples were found to be 0.043 (low), 0.98 and 3.7% (high) by weight. For the phase transition study, Ka-band EPR spectra were performed in the (110) plane of the crystal with the magnetic field direction along the g_{max} (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 determining the onset of the phase transition is highest in this direction because of the appearance of as many as six lines with the largest magnetic field separations (De et al., 1984).

Above T_{c1} , the EPR spectrum consists of an isotropic line only. It may be mentioned that it is not possible to determine the phase transition along the (111) direction because all the EPR lines remain coincident 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

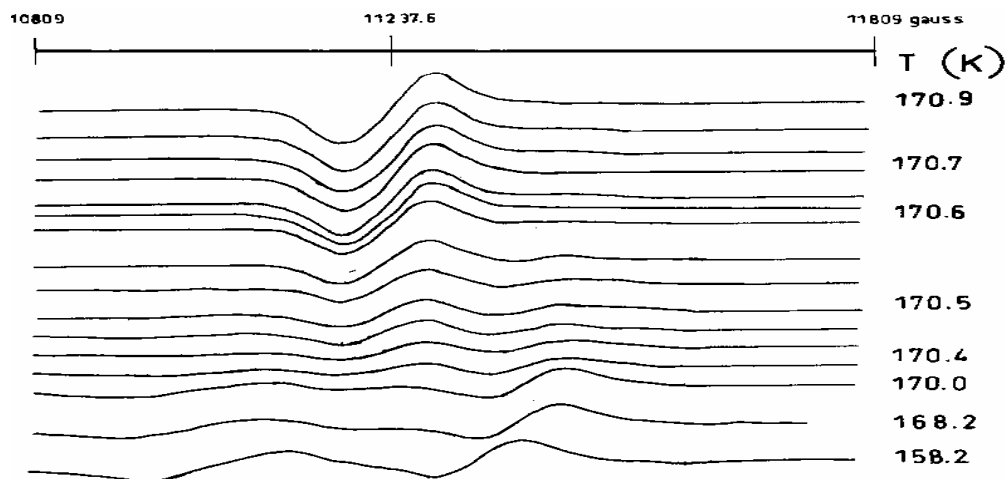


Figure 1. EPR spectra of ZTFH: Cu^{2+} recorded in the immediate neighbourhood of the phase transition temperature T_{ci} for a Cu^{2+} concentration of 0.043 wt%.

spectrometer built in the laboratory. Temperatures were varied by manual control. An approximately uniform cooling and heating rate of $1^\circ\text{C}/\text{min}$ to $1^\circ\text{C}/120\text{ min}$ could be attained. The sample could be maintained at any temperature above 77 K to within $\pm 0.1^\circ\text{C}$ for 30 min. The temperature of the sample structure was measured by both E- and T- type thermocouples with digital readout. The thermocouple and the digital readouts were calibrated at the standard temperatures of liquid N_2 , solid CO_2 , a toluene and liquid N_2 slush and a mixture of isopropane and solid CO_2 .

Precise determination of transition temperature

The transition temperature was obtained by recording the variation in the intensity I of the isotropic signal as the sample was cooled at a uniform rate of $3^\circ\text{C}/\text{h}$ down to about 1°C above the phase transition. The sample is then cooled at a rate of $0.5^\circ\text{C}/\text{h}$ for Cu^{2+} concentration up to 1.81% by wt. and at a rate $1.5^\circ\text{C}/\text{h}$ for Cu^{2+} concentration higher than 1.81% by wt. The spectra were then run with a magnetic field sweep time of 5 min. The sample was kept in vacuum during the entire experiment, to prevent moisture accumulation on the sample. T_{ci} during cooling ($T_{ci\downarrow}$) can be noted by the appearance of the high-field lines or by noticeable reduction (with all the spectrometer parameters remaining constant) in the isotropic EPR signal intensity I (as high as 60% in crystal with low impurity concentration with a temperature variation of $\pm 0.1^\circ\text{C}$). In Figure 1 which corresponds to a sample containing 0.043% (by wt) Cu^{2+} , it can be seen that at 170.4 K there is a noticeable change in I from that at 170.5 K. This is accompanied by the appearance of high-field signals, which is prominent at 170.3 and 170.2 K. So, $T_{ci\downarrow}$ for this Cu^{2+} concentration (that is, 0.043% by wt.) could be recorded as $170.4 \pm 0.2\text{ K}$ ($\pm 0.1\text{ K}$ is the error in the temperature recording). It can be seen that both the high and the low-temperature phases coexist over a finite temperature, ΔT . In this investigation ΔT_c is found to be dependent on the concentration of the impurity. Figure 2 shows a similar recording for a higher Cu^{2+} ion concentration (3.7 wt.%).

During warming from the 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 1), $T_{ci\uparrow}$ during warming from the low temperature phase is found to be slightly higher than the transition temperature $T_{ci\downarrow}$ during cooling from the trigonal phase. This hysteresis is due to the co-existence of the two phases as mentioned earlier. Relaxation between the two phases may also be responsible for the said observed differences. The $T_{ci\downarrow}$ and $T_{ci\uparrow}$ of ZTFH crystal are shown in Table 1 for various Cu^{2+} concentrations. It is seen from Table 1 that phase transition temperature T_{ci} decreases with Cu^{2+} impurity concentration. The value of the transition temperature T_{ci} obtained by this method is found to be independent of orientation of the magnetic field.

RESULTS AND DISCUSSION

Jahn-Teller potential well energy splitting

In Figure 1 we see that for low Cu^{2+} concentration the phase transition is very sharp with respect to change of temperature while from Figure 2 we see that for high concentration the phase transition is gradual with respect to change of temperature. As the Cu^{2+} concentration increases it is observed that the transition becomes more and more gradual. Let us see how such observation yields the JT potential well splitting, E_0 (Figure 3).

In our earlier work (De et al., 1984; De, 1986) it was conjectured that one of the Jahn-Teller potential well is lowered with respect to the other wells (Figure 3) at, or, immediately below the phase transition temperature T_{ci} . The intensity of the isotropic EPR signal above T_{ci} suddenly drops at T_{ci} and the isotropic signal vanishes in a small temperature interval below T_{ci} for low Cu^{2+} concentration. The spin-lattice relaxation rate $1/T_1$ at T_{ci} is found from equation (6) of (De, 1986) to be $6 \times 10^6\text{ s}^{-1}$. Using the approximate R value found by Dang et al.

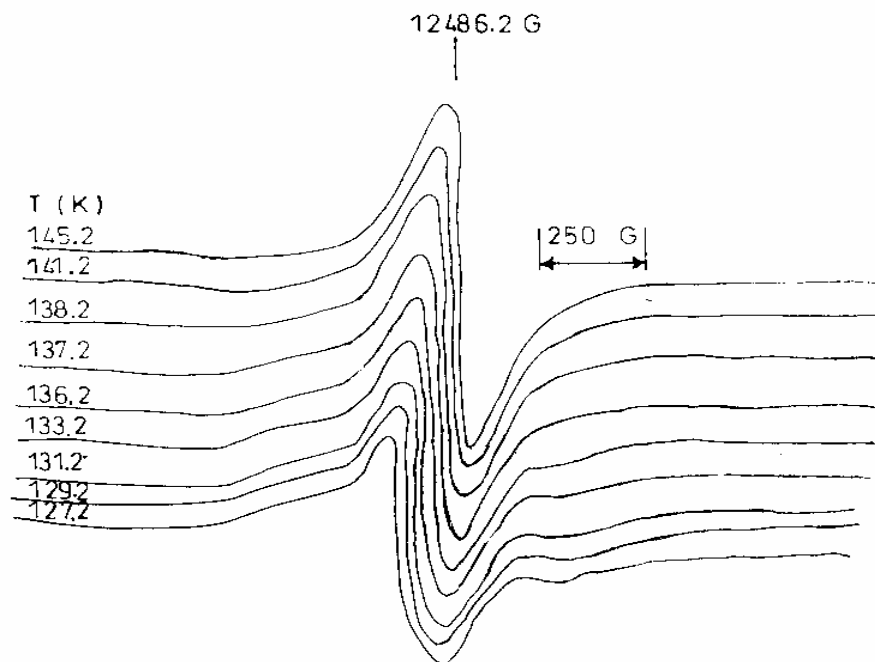


Figure 2. The EPR spectrum recorded for a Cu^{2+} concentration of 3.7 wt% in ZTFH. It is seen that the transition to the monoclinic phase (see text) takes place gradually with respect to the change in temperature in contrast with the sharp transition observed for low Cu^{2+} concentrations (Figure 1).

Table 1. Observed change in phase transition temperature ($\Delta T_{cl} = T_{c0} - T_{c1}$) in $\text{ZnTiF}_6 \cdot 6\text{H}_2\text{O}$ for varying Cu^{2+} ion impurity concentration, T_{c0} for pure lattice = 182K.

Concentration*,c Fraction Wt%±0.01	Atomic X	On cooling $\Delta T_{cl} \pm \delta$ (K) ¹	On warning $\Delta T_{cl} \pm \delta$ (K) ¹
0.043	0.0053	11.0	9.8
0.38	0.0195	14.1	11.0
0.50	0.0227	15.4	12.9
0.63	0.0317	16.0	14.1
0.69	0.0370	17.3	15.4
0.94	0.0495	19.1	17.3
1.06	0.0528	20.4	17.9
1.44	0.0723	26.3	24.4
1.81	0.0950	27.9	26.3
3.70	0.1952	41.0	38.8
8.94	0.4710	71.0	-----

The concentration is determined spectroscopically by Galbraith Analytical Laboratories Inc., Tennessee, USA, with the given accuracy. For $0 < c < 1.06$, $0.2 < \delta < 1$; $1.06 < c < 1.81$, $1 < \delta < 2$; $c = 3.7$, $2 < \delta < 3$; $c = 8.94$, $5 < \delta < 6$.

(1974) of $(1/T_i)/(1/\tau) = 6.4 \times 10^{-3}$ for the (100) direction in $\text{Cu}^{2+}:\text{ZnSiF}_6 \cdot 6\text{H}_2\text{O}$, we can approximately estimate the value of the tunneling rate $1/\tau$ at T_{cl} in the $\text{Cu}^{2+}:\text{ZTFH}$ to

be $0.94 \times 10^9 \text{ s}^{-1}$, much less than the microwave frequency of 35 GHz employed in this work. We can also approximately estimate approximately this tunneling rate

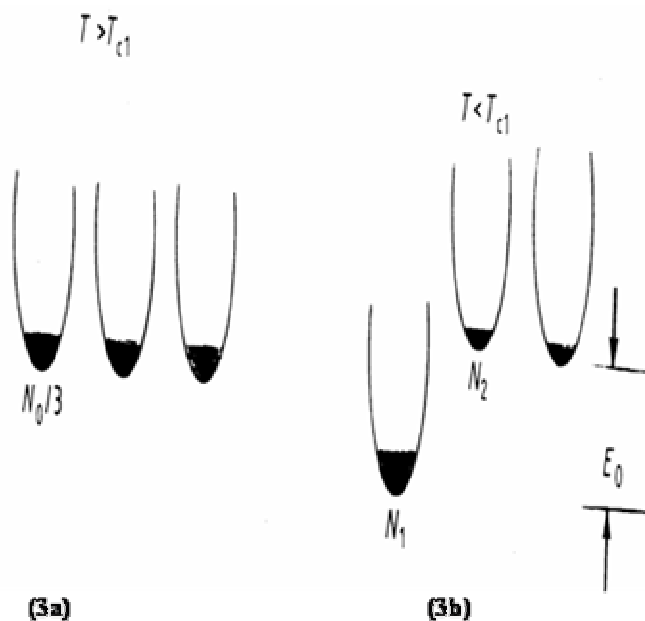


Figure 3. Schematic picture showing that the JT potential wells are non-equivalent by an energy E_0 below T_{cl}

in dilute sample from the observed linewidth ($\Delta H = 115$ G) before transition using the equation $g\mu_B\Delta H = h/\tau$. The corresponding $1/\tau$ is $0.30 \times 10^9 \text{ s}^{-1}$ which is again much less than 35 GHz. Therefore, when the measurement is made along one of the three (100) directions, the isotropic EPR signal intensity, $I_{+\delta}$ at $T = T_{cl} + \delta$ ($\delta = -0.1\text{K}$) is proportional to the ground-state population of the 2A_2 state (O'Brien and Chancey, 1993) in one of the wells in Figure 3a, that is,

$$\lim_{\delta \rightarrow 0} (I_{+\delta}) = CN_0/3$$

N_0 is the total population of the 2A_2 state which gives rise to the isotropic signal in the present system (De, 1986).

The intensity of the isotropic signal $I_{-\delta}$, at $T = T_{cl} - \delta$ is governed by the population, N_2 of the upper two wells (Figure 3b), which is given by

$$N_2 = N_0 \exp(-E_0/kT) / (1 + 2\exp(-E_0/kT)) \quad (1)$$

Thus:

$$\lim_{\delta \rightarrow 0} (I_{-\delta}/I_{+\delta}) = 3x/(1+2x)$$

$$\text{Where } x = \exp(-E_0/kT) \quad (2b)$$

Using equations (2a and 2b), it is possible to determine E_0 at different temperatures from EPR spectra imme-

diately below T_{cl} for low Cu^{2+} concentration in ZTFH (Tables 2a and 2b). However, at high Cu^{2+} concentration (Figure 2), the isotropic signal continues over a broad temperature range below T_{cl} . In order to compute E_0 well below T_{cl} , from the isotropic signal intensity, $I_{T_{cl}}$ - we rely on the fact that $I_{T_{cl}}$ is proportional to N_2 and thus the following equations were used to determine E_0 at temperatures below T_{cl} of a ZTFH crystal containing a high Cu^{2+} concentration (Figure 2).

$$I_{T_{cl}} / I_{-\delta} = x(1+2x_1)/x_1(1+2x), \quad (3a)$$

Where

$$x_1 = \exp(-E_{01}/kT), \text{ with } T \approx T_{cl} \quad (3b)$$

Here, E_{01} corresponds to the energy value calculated using equations (2a and 2b) at the temperature (close to T_{cl}), when the decrease in the intensity of the isotropic signal, I_0 is just observed. $I_{T_{cl}}$ is the intensity at a given temperature, T below T_{cl} . The computed values of E_0 at different temperatures are given in Table 3.

It is apparent from our results (Tables 1 - 3) that while E_0 increases rapidly within a small temperature interval below T_{cl} for a sample containing low Cu^{2+} concentrations, for higher Cu^{2+} concentration in ZTFH, E_0 increases below T_{cl} over a broader temperature interval (Table 3) than that for lower concentrations. The rate of increase

Table 2. Temperature variation of the Jahn-Teller potential energy splitting in ZTFH for low Cu²⁺ concentration (a) 0.043% wt (b) 0.98%wt.

Temperature (K) ± 0.1K	E ₀ (cm ⁻¹) ± 6
170.5	81
170.4	114
170.3	135
170.2	144

(a)

Temperature (K) ± 0.1K	E ₀ (cm ⁻¹) ± 6
164.4	99
164.3	114
164.2	124
164.1	131

(b)

Table 3. Temperature variation of the Jahn-Teller potential well energy splitting in ZTFH for Cu²⁺ concentration (3.7% wt).

Temperature (K) ±1	E ₀ (cm ⁻¹) ±8
141	22
138	44
137	53
136	66
133	75
131	86
129	89
127	92

gradually diminishes as the sample is cooled well below T_{cl} . For low Cu²⁺ concentrations (Tables 2a and b), most of the increase in E_0 takes place within a narrow temperature interval (~1K), which is much smaller than the interval predicted by previous workers (Rubins and Drumheller, 1987) and at rates much higher than that for high Cu²⁺ concentration. From Tables 1 - 3 it appears that the value of E_0 tends to attain the saturation value of potential well splitting at temperatures much higher than those determined independently (from the temperature variation of the $g_{||}$ and g_{\perp})¹⁷. From Tables 2a and b we see that E_0 decreases with Cu²⁺ concentration. It is consistent with the observation that T_c decreases with Cu²⁺ concentration (Table 1). The Jahn-Teller potential well splitting, E_0 can be taken as a measure of the monoclinic distortion in this crystal and thus it appears that the rate of progress of this distortion below T_{cl} might depend on Jahn-Teller impurity concentration in ZnTiF₆.6H₂O. It is to be noted that for low Cu²⁺ concentrations, the phase transition of the host lattice is first order (as reflected by sudden abrupt change in the EPR signal intensity at T_{cl} upon cooling) like that of the pure lattice⁴; whereas with the increase of the impurity concentration, the EPR signal intensity starts decreasing at T_{cl} slowly and continuously upon cooling. This is

indicative of gradual change of the order of phase transition of the impurity doped lattice as the concentration is increased. As mentioned earlier the energy splitting E_0 is a result of the monoclinic distortion at T_{cl} . In Cu²⁺:ZnSiF₆.6H₂O, where there is no phase transition, the JT potential wells are equivalent (that is, no energy splitting) with $E_0 = 0$ down to the lowest temperatures. Our findings indicate that as the JT impurity concentration is increased the saturation of the monoclinic distortion would take place at lower and lower temperature. The question that would naturally emerge from the analysis is that phase transition cease to exist in Cu²⁺:ZnTiF₆.6H₂O for Cu²⁺ concentration above certain limit?. The soft mode of the host lattice is modified as a result of coupling with the JT active modes (which in the present case corresponds to the vibronic modes of [Cu²⁺, H₂O]). It is then possible that this could give rise to a reduction in the barrier to [TiF₆]²⁻ reorientation (see introduction). At T_{cl} the barrier to [TiF₆]²⁻ reorientation is increased. From the results (Tables 2 – 3) we can say that the saturated value of E_0 tends to decrease with increase of Cu²⁺ concentration. If the barrier height is reduced as a result of the said interaction which is expected to increase with Cu²⁺ concentration, the rotation of the fluorine octahedra, [TiF₆]²⁻ would then persist in the impurity doped crystal even below T_{cl} of the host lattice, as if the phase transition temperature is lowered. The barrier height reduction in Cu²⁺:ZnTiF₆.6H₂O for Cu²⁺ is also supported by the fact that the trigonal phase exists below T_{cl} of the host lattice as evident by the isotropic EPR signal existing at and below the new T_{cl} [12]. Thus, there appears to be one to one correspondence between the barrier height of phase transition and E_0 in Cu²⁺:ZnTiF₆.6H₂O crystals. We may understand the change of E_0 with temperature (as obtained in this crystal) to be due to change of order parameter of phase transition with temperature, the order parameter being the barrier to [TiF₆]²⁻ rotation. As seen from Tables 2 - 3, E_0 might be negligibly small for Cu²⁺ concentration above certain limit. This would then mean that the barrier height is also vanishing for such concentration of Cu²⁺ ions. The phase transition of the host lattice would then cease to exist. In fact, the non-exis-

tence of any phase transition (in the interval 300-0K) in $\text{CuTiF}_6 \cdot 6\text{H}_2\text{O}$ crystal can now be understood in this light.

Estimation of the change of transition temperature (ΔT_c) with atomic fraction, x , of Cu^{2+} impurity in $\text{Zn}_{1-x}\text{Cu}_x\text{TiF}_6 \cdot 6\text{H}_2\text{O}$ crystals

The theoretical estimation of the change of T_c with impurity concentration in a host lattice is still a challenge. The observed lowering of T_{cl} in Cu^{2+} doped ZTFH with Cu^{2+} concentration (Table 1) may be attributed to the increase in soft mode frequency (ω_0) as a result of impurity doping (Shields et al., 1992; De, 2002; Oguama et al., 1997). The corresponding modification has at least the following components: (i) A change in ionic mass changes the soft mode frequency, which in turn changes T_c . (ii) A change in ionic radius can introduce a change in lattice distortions and / or strains, which are expected to be localized, especially for low impurity concentration. (iii) If the impurity ion exhibits a Jahn-Teller effect like that in the present case, then an additional change in soft mode frequency occurs due to coupling of the soft mode with Jahn-Teller modes of the $[\text{Cu}^{2+}, 6\text{H}_2\text{O}]$ ligand cluster. This would modify the phase transition behavior of the host lattice significantly from that without the impurity (Oguama et al., 1997). (iv) Considering all such contributions, the resultant soft mode frequency ω can be expressed in terms of the soft mode frequency, ω_0 of the pure lattice and atomic fraction, x of the impurity ion, in $[\text{Cu}_x\text{Zn}_{1-x}\text{TiF}_6 \cdot 6\text{H}_2\text{O}]$ single crystal,

$$\omega^2 = \omega_0^2 + f(\omega_0, x) \quad (a)$$

The functional dependence can be evaluated by taking the above three factors into consideration in addition to the soft mode frequency ω_0 and the masses of ions such as Cu^{2+} , Zn^{2+} , Ti^{4+} , F and H_2O .

Now according to Landau's mean field theory

$$\omega_0^2 = K(T - T_{co}) \quad (b)$$

For low Cu^{2+} concentration in Table 1, following Oguama et al. (1997) method

$$\omega^2 = K(T - T_{co}) = K(T - T_{co} + \Delta T_c) = \omega_0^2 + K\Delta T_c \quad (c)$$

$$\Delta T_c = T_{co} - T_{c1}$$

T_{co} is the phase transition temperature, T_{c1} of the pure lattice; ΔT_c is the change in phase transition temperature T_{c1} due to atomic fraction x of the impurity ion. From equations (a) - (c) we get

$$\Delta T_c = f(\omega_0, x) / K \quad (d)$$

When $f(\omega_0, x)$ is theoretically known, then the mean field constant K can be evaluated by using one observed value of ΔT_c for a given x . ΔT_{cs} for other values of x (Table 1) can then be evaluated from equation (d) and compared with the observed values. Deviation from Landau's mean-field theory, if any in the present system can be taken into account following the procedure in (De, 2002). Such theoretical calculations are in progress. For high Cu^{2+} concentration in Table 1 (say from 3.81% and above) the quantitative explanation of T_{cl} with x may necessitate a change in K due to the lattice distortion which is going to be appreciable at high impurity concentration.

Conclusions and Recommendations

In this study, we have clearly focused on the Cu^{2+} impurity concentration dependence of the behavior of E_0 with temperature as the single crystal of $\text{Cu}^{2+}:\text{ZnTiF}_6 \cdot \text{H}_2\text{O}$ is cooled below T_{cl} . This has been neglected by previous researchers (Ziatdinov et al., 1983; Rubins and Drumheller, 1987). The values of the energy E_0 , the lowering of one of the JT potential wells with respect to the other two in $\text{Cu}^{2+}:\text{ZnTiF}_6 \cdot 6\text{H}_2\text{O}$ single crystal below T_{cl} are obtained at temperatures immediately below T_{cl} for various Cu^{2+} concentrations from the EPR spectra. E_0 and its temperature dependence immediately below T_{cl} and T_{cl} itself are found to depend significantly on Cu^{2+} ion concentration in ZTFH. When the sample is cooled, it is discovered that for high Cu^{2+} concentration, E_0 increases below T_{cl} at a rate much slower than that for low concentration and over a broader temperature range. This appears to have a bearing on the monoclinic distortion that proceeds in this crystal below T_{cl} . The lowering of one of the JT potential wells below the other two does not occur in some JT systems (Dang et al., 1974; Shields et al., 1992) that do not exhibit structural phase transition. The energy E_0 is a measure of the monoclinic distortion below T_{cl} in such impurity doped crystals where structural phase transitions coexist with Jahn-Teller effect. To provide further validation these observations made on E_0 in this study, E_0 may further be evaluated independently employing other techniques, such as far IR absorption, and NMR studies of this crystal for low and high Cu^{2+} concentrations at temperatures in the immediate vicinity of T_{cl} , and the new results be compared with the results and inferences in this work. A qualitative explanation of the observed change of T_{c1} with Cu^{2+} concentration is provided. We are yet to arrive at the theoretical understanding of the observed change.

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