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

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The energy \( E_0 \) by which one of the three Jahn-Teller potential wells becomes lower than the other two in \( \text{Cu}^{2+}:\text{ZnTiF}_6.6\text{H}_2\text{O} \) single crystal at phase transition temperature, \( T_{cl} \) are determined at temperatures below \( T_{cl} \) for different \( \text{Cu}^{2+} \) concentrations from the electron paramagnetic resonance (EPR) spectra. As the sample is cooled, it is found that for high \( \text{Cu}^{2+} \) concentration, \( E_0 \) 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 \( \text{Cu}^{2+} \) 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 \( \text{Cu}^{2+} \) impurity concentration is presented. \( E_0 \) is negligibly small for \( \text{Cu}^{2+} \) concentrations above certain limits means that the barrier height is also vanishing for such \( \text{Cu}^{2+} \) concentrations that is, phase transition of host lattice ceases. This is likely the reason for non-existence of phase transition in some compounds like \( \text{CuTiF}_6.6\text{H}_2\text{O} \) and \( \text{ZnSiF}_6.6\text{H}_2\text{O} \) belonging to the same class with \( \text{ZnTiF}_6.6\text{H}_2\text{O} \).

Key words: \( \text{ZnTiF}_6.6\text{H}_2\text{O} \), \( \text{Cu}^{2+} \), 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 \( \text{CaCd(\text{CH}_3\text{OO})_4.6}\text{H}_2\text{O} \) single crystals for different \( \text{Cu}^{2+} \) 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 \( \text{ABF}_6.6\text{H}_2\text{O} \) (\( A = \) a divalent metal, \( B = \) a tetravalent metal, Ti, Si, Ge, etc.), the crystal zinc fluotitanate hexahydrate, \( \text{ZnTiF}_6.6\text{H}_2\text{O} \) (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 systems.
A(H2O)6 and BF6 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; Syomaya and Osaki, 1972).

19F NMR studies (Afanasayev et al., 1979) reveal a first-order phase transition at 182 K(Tcl) when the rotation of the fluorine octahedra freezes and the single 19F line splits into two, indicating the loss of a chemical equivalence between the fluorine atoms, following a tetragonal distortion of the [TiF6]2- octahedra. However, at Tcl, no appreciable change in the 1H resonance was observed and accordingly they postulated that a change in the [Zn(6H2O)]2+ symmetry caused a sudden transition in ZnTiF6.6H2O. A weak transition of a continuous nature at 217 K(Tc2) 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 [M2+,H2O] 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 [TiF6]2- and [M2+,H2O] octahedra. Bose et al.'s 2H NMR studies (Bose et al., 1983; 1987) in ZnTiF6.6H2O 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.

Cu2+ ion in ZTFH has an orbitally degenerate 2E ground state. De et al (1984) detailed EPR studies on Cu2+ doped ZTFH revealed that the Cu2+ ions in this system exhibit a strong Jahn-Teller effect as expected (O'Brien and Chancey, 1993). With a low Cu2+ concentration of 0.043% weight (% wt), the transition temperature, Tcl was lowered by 110°C from that (182 K) of pure ZTFH; and further lowering in Tcl 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 Mn2+ concentration. In contrast to the said lowering of Tcl, they found that Mn2+ ion in this crystal increases the Tcl, in common with other measurements in ZnGeF6.6H2O Ziatdinov et al., 1983).

The JT stabilization energy EJT = 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 parameters gµ, gλ, Aµ, Aλ 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, Eo, 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 Cu2+ in ZnTiF6.6H2O. Later, Rubins and Drumheller (1987) carried out a further study of the EPR spectrum of Cu2+ in ZnTiF6.6H2O between 4 K and 160 K and concluded that for low Cu2+ concentration, E0 has small temperature dependence below Tcl.

It is to be noted that such lowering of potential well does not occur in Cu2+-ZnSiF6.6H2O 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: Cu2+:La2Mg3(NO3)12.D2O, Cu2+:(BrO3)2.6H2O (Breen et al., 1969), etc. Eo in Cu2+:ZnTiF6.6H2O, or Cu2+:ZnGeF6.6H2O can be taken as a measure of the monoclinic distortion below Tcl in these crystals. However, previous studies have not clearly focused on the impurity concentration dependence of the behavior of Eo with temperature as the sample is cooled well below Tcl. In this study we have tried to address this issue together with the nature of dependence of phase transition temperature (Tcl) on Cu2+ ion impurity concentration in ZTFH.

EXPERIMENTAL

Single crystals of ZTFH were grown by slow evaporation of an aqueous solution of ZnTiF6 obtained by dissolving ZnCO3 in 40% H2TiF6. CuCO3 was added to grow doped crystal of various Cu2+ concentrations. Re-crystallization was carried out to reduce the Mn2+ impurity concentration beyond the EPR detection limit in all of the crystals investigated with varying Cu2+ 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 Tcl s were obtained from EPR experiments) were analyzed by Galbraith Laboratories, Tennessee, USA using standard spectroscopic technique for estimation of the impurity concentration. The Cu2+ 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_i direction or (100) direction of the Cu2+ 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 Tcl, 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...
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 °C/min to 1 °C/120 min could be attained. The sample could be maintained at any temperature above 77 K to within ±0.1 °C for 30 min. The temperature of the sample structure was measured by E- and T-type thermocouples with digital readout. The standard temperatures of liquid $N_2$, solid $CO_2$, a toluene and liquid $N_2$ slush and a mixture of isopropane and solid $CO_2$.

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 $T_{cl}$. The intensity of the isotropic EPR signal above $T_{cl}$ suddenly drops at $T_{cl}$ and the isotropic signal vanishes in a small temperature interval below $T_{cl}$ for low $Cu^{2+}$ concentration. The spin-lattice relaxation rate $1/T_1$ at $T_{cl}$ is found from equation (6) of (De, 1986) to be $6x10^8$ 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 ZnTiF$_6$6H$_2$O for varying Cu$^{2+}$ ion impurity concentration, $T_{c0}$ for pure lattice =182K.

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

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 $(1/T_1)/(1/\tau)=6.4\times10^{-3}$ for the (100) direction in Cu$^{2+}$:ZnSiF$_6$6H$_2$O, we can approximately estimate the value of the tunneling rate $1/\tau$ at $T_{cl}$ in the Cu$^{2+}$: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.
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 $0.30 \times 10^9$ 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 $T = T_{cl} + \delta$ ($\delta = -0.1K$) 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,

$$\lim_{\delta \to 0} (I_{\delta} / I_0) = CN_0/3$$

$N_0$ 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

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

(1)

Thus:

$$\lim_{\delta \to 0} (I_{\delta} / I_0) = 3x/(1+2x)$$

(2a)

Where $x = \exp(-E_0/kT)$

(2b)

Using equations (2a and 2b), it is possible to determine $E_0$ at different temperatures from EPR spectra immediately 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 ZFTH crystal containing a high Cu$^{2+}$ concentration (Figure 2).

$$I_{T_{cl}} / I_{\delta} = x(1+2x_i)/x_i(1+2x)$$

(3a)

Where

$$x_i = \exp(-E_0/kT), \text{ with } T = \sim T_{cl}$$

(3b)

Here, $E_0$ 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...
gradually diminishes as the sample is cooled well below $T_{cl}$. For low $\text{Cu}^{2+}$ concentrations (Tables 2a and b), most of the increase in $E_0$ takes place within a narrow temperature interval ($\sim 1$K), which is much smaller than the interval predicted by previous workers (Rubins and Drumheller, 1987) and at rates much higher than that for high $\text{Cu}^{2+}$ 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 $g_i$ and $g_j$)\(^{17}\). From Tables 2a and b we see that $E_0$ decreases with $\text{Cu}^{2+}$ concentration. It is consistent with the observation that $E_0$ decreases with $\text{Cu}^{2+}$ 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 $\text{ZnTiF}_6\cdot6\text{H}_2\text{O}$. It is to be noted that for low $\text{Cu}^{2+}$ 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 lattice\(^4\); 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 $\text{Cu}^{2+}::\text{ZnSiF}_6\cdot6\text{H}_2\text{O}$, 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 $\text{Cu}^{2+}::\text{ZnTiF}_6\cdot6\text{H}_2\text{O}$ for $\text{Cu}^{2+}$ 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 $[\text{Cu}^{2+}, \text{H}_2\text{O}]$). It is then possible that this could give rise to a reduction in the barrier to $[\text{TiF}_6]^{2-}$ reorientation (see introduction). At $T_{cl}$ the barrier to $[\text{TiF}_6]^{2-}$ 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 $\text{Cu}^{2+}$ concentration. If the barrier height is reduced as a result of the said interaction which is expected to increase with $\text{Cu}^{2+}$ concentration, the rotation of the fluorine octahedra, $[\text{TiF}_6]^{2-}$ 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 $\text{Cu}^{2+}::\text{ZnTiF}_6\cdot6\text{H}_2\text{O}$ for $\text{Cu}^{2+}$ 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 $\text{Cu}^{2+}::\text{ZnTiF}_6\cdot6\text{H}_2\text{O}$ 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 $[\text{TiF}_6]^{2-}$ rotation. As seen from Tables 2 - 3, $E_0$ might be negligibly small for $\text{Cu}^{2+}$ concentration above certain limit. This would then mean that the barrier height is also vanishing for such concentration of $\text{Cu}^{2+}$ ions. The phase transition of the host lattice would then cease to exist. In fact, the non-exis-

Table 2. Temperature variation of the Jahn-Teller potential energy splitting in ZTFH for low $\text{Cu}^{2+}$ concentration (a) 0.043% wt (b) 0.98%wt.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$E_0$ (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>± 0.1K</td>
<td>± 6</td>
</tr>
<tr>
<td>170.5</td>
<td>81</td>
</tr>
<tr>
<td>170.4</td>
<td>114</td>
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<td>170.3</td>
<td>135</td>
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<td>170.2</td>
<td>144</td>
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</table>

(a)

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$E_0$ (cm(^{-1}))</th>
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<tbody>
<tr>
<td>± 0.1K</td>
<td>± 6</td>
</tr>
<tr>
<td>164.4</td>
<td>99</td>
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<td>164.3</td>
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<td>124</td>
</tr>
<tr>
<td>164.1</td>
<td>131</td>
</tr>
</tbody>
</table>

(b)

Table 3. Temperature variation of the Jahn-Teller potential well energy splitting in ZTFH for $\text{Cu}^{2+}$ concentration (3.7% wt).

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$E_0$(cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>±1</td>
<td>±8</td>
</tr>
<tr>
<td>141</td>
<td>22</td>
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<td>44</td>
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<td>129</td>
<td>89</td>
</tr>
<tr>
<td>127</td>
<td>92</td>
</tr>
</tbody>
</table>
tence of any phase transition (in the interval 300-0K) in CuTiF₆.6H₂O crystal can now be understood in this light.

Estimation of the change of transition temperature (ΔTc) with atomic fraction, x, of Cu²⁺ impurity in Zn₆CuₓTiF₆.6H₂O 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_c in Cu²⁺ doped ZTFH with Cu²⁺ concentration (Table 1) may be attributed to the increase in soft mode frequency (ω₀) as a result of impurity doping (Shield 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 [Cu²⁺, 6H₂O] 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, ω₀, of the pure lattice and atomic fraction, x, of the impurity ion, in [CuₓZn₆−ₓTiF₆.6H₂O] single crystal,

\[ \omega^2 = \omega_0^2 + f(\omega_0, x) \]  

(a)

The functional dependence can be evaluated by taking the above three factors into consideration in addition to the soft mode frequency ω₀ and the masses of ions such as Cu²⁺, Zn²⁺, Ti⁴⁺, F and H₂O.

Now according to Landau’s mean field theory

\[ \omega_0^2 = K(T-T_{c0}) \]  

(b)

For low Cu²⁺ concentration in Table 1, following Oguama et al. (1997) method

\[ \omega^2 = K(T-T_{c0}) = K(T-T_{c0}+\Delta T_c) = \omega_0^2 + K\Delta T_c \]  

(c)

\[ \Delta T_c = T_{c0} - T_{c1} \]

T_c₀ 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

\[ \Delta T_c = f(\omega_0, x)/K \]  

(d)

When f(ω₀, 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_c 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 Cu²⁺ concentration in Table 1 (say from 3.81% and above) the quantitative explanation of T_c 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 Cu²⁺ impurity concentration dependence of the behavior of E₀ with temperature as the single crystal of Cu²⁺:ZnTiF₆.6H₂O is cooled below T_c. This has been neglected by previous researchers (Ziatdinov et al., 1983; Rubins and Drumheller, 1987). The values of the energy E₀, the lowering of one of the JT potential wells with respect to the other two in Cu²⁺:ZnTiF₆.6H₂O single crystal below T_c are obtained at temperatures immediately below T_c for various Cu²⁺ concentrations from the EPR spectra. E₀ and its temperature dependence immediately below T_c and T_c itself are found to depend significantly on Cu²⁺ impurity concentration in ZTFH. When the sample is cooled, it is discovered that for high Cu²⁺ concentration, E₀ increases below T_c 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_c. 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 E₀ is a measure of the monoclinic distortion below T_c in such impurity doped crystals where structural phase transitions coexist with Jahn-Teller effect. To provide further validation these observations made on E₀ in this study, E₀ may further be evaluated independently employing other techniques, such as far IR absorption, and NMR studies of this crystal for low and high Cu²⁺ concentrations at temperatures in the immediate vicinity of T_c, and the new results be compared with the results and inferences in this work. A qualitative explanation of the observed change of T_c with Cu²⁺ concentration is provided. We are yet to arrive at the theoretical understanding of the observed change.

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