EPR studies of phase transitions in cadmium calcium acetate hexahydrate as a function of different paramagnetic impurity-ion concentrations

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The phase transition in cadmium calcium acetate hexahydrate (CCDAH) has been studied in detail with electron paramagnetic resonance (EPR) as a function of two different paramagnetic ion concentrations, namely, Cu^{2+} and Mn^{2+} ions. The change in transition temperature (122–143 K) with Cu^{2+} ion concentrations is explained in terms of mean-field theory and a soft vibrational mode of the -Ca-$Cd_{1-x}Cu_x$-Ca- chain along the c axis of the crystal. While the same theory can also explain our observed transition temperature (118–128 K) as a function of the Mn^{2+} ion concentration in this crystal, it does not explain why the limiting value of the transition temperature (i.e., 145 K) of $CaCd_{1-x}Cu_x(CH_3COO)_4 \cdot 6H_2O$ as x tends to zero, is strikingly different from the limiting value of (~ 128.4 K) of $CaCd_{1-x}Mn_x(CH_3COO)_4 \cdot 6H_2O$ as x tends to zero. The same theory also successfully explains the absence of any phase transition in isomorphous $CaCu(CH_3COO)_4 \cdot 6H_2O$. The value of $-dT_c/dx$ is significantly higher with Mn^{2+} than with Cu^{2+} in CCDAH. [S0163-1829(97)01329-5]

I. INTRODUCTION

The usefulness of the electron paramagnetic resonance (EPR) technique in elucidating the magnetic properties of a substitutional paramagnetic ion and the local crystal-field symmetry surrounding the ion when the ion is embedded in a crystalline lattice, is well known.[1–4] The size and effective valency of the substitutional paramagnetic ion should match that of the nonmagnetic host lattice. EPR is observed when a high-frequency magnetic field induces transitions between the Zeeman splittings of magnetic ions or defects placed in an external magnetic field, H. The condition $g\mu_B H = h\nu$ holds in general for EPR. Here, g is the spectroscopic splitting factor of the ion, which may depend on the orientation of H with respect to the symmetry axes of the crystal or ligand field of the ion, μ_B is the Bohr magneton, and h is Planck's constant. EPR is a very sensitive tool in studying phase transitions[5–7] and the Jahn-Teller effect.[8] The order parameter can be determined from EPR measurements for displacive and order-disorder systems.[7]

The crystal structure of cadmium calcium acetate hexahydrate, $CaCd(CH_3COO)_4 \cdot 6H_2O$ (CCDAH), is isomorphous with that of copper calcium acetate hexahydrate (CCAH). The latter crystal (i.e., CCAH), is not known to exhibit any structural phase transition within the temperature range 350–1.2 K.[9] However, replacement of copper by the larger cadmium ion introduces a phase transition in this crystal. The temperature of the phase transition, T_c, is found to be 145 K (Ref. 10) by EPR studies, using a Cu^{2+} ion as a probe. The studies revealed that the phase-transition temperature of $CaCd_{1-x}Cu_x(CH_3COO)_4 \cdot 6H_2O$ varies from 144 to 124 K as the atomic concentration of copper varies from 0.07% ($x = 0.005$) to 1.32% ($x = 0.1022$) of the sample weight, where x is the atomic fraction of Cu^{2+}. A similar observation was made by Sikdar and Pal[11] who reported that T_c ranges from 140 K in a sample containing 0.5% copper to 128 K in a sample whose concentration was not specified. The metal ions at $T > T_c$ lie along the c axis, while for $T < T_c$ they are

believed to have a zigzag pattern along the c axis leading to an orthorhombic distortion.

In an earlier study, De[12] has demonstrated that T_c in a zinc fluotitanate hexahydrate (ZNTFH) crystal is sensitive to the Cu^{2+} and Ni^{2+} probe concentrations. The transition, which occurs over a temperature interval as small as ± 0.1 °C about T_c (first-order transition) for low Cu^{2+} concentration (0.07% of sample weight), becomes very gradual with respect to temperature change when the concentration is high. Moreover, De observed by the EPR technique that the Cu^{2+} ion in ZNTFH introduces a significantly larger change in T_c than that caused by Ni^{2+} of similar concentration.[12] The question that now arises is how does a paramagnetic ion modify the phase transition of a nonmagnetic host lattice? The following points relating to these results are noteworthy.

(i) The change in ionic mass changes the soft mode frequency and this provides a large contribution towards the change in T_c.

(ii) The ionic radii and masses of Ni^{2+} and Cu^{2+} ions are not significantly different from that of Zn^{2+} in ZNTFH, whereas Cu^{2+} and Mn^{2+} are significantly different from that of the Cd^{2+} ion in CCDAH. A change in ionic radius can introduce a change in lattice distortions and/or strains, which are expected to be localized especially for low concentration. From the experimental results cited above, this contribution to a change in T_c is expected to be smaller than that of (i). In fact, as will be seen later, (i) alone can fairly well explain quantitatively the change in T_c of $CaCd_{1-x}Cu_x(CH_3COO)_4 \cdot 6H_2O$ as a function of x.

(iii) Cu^{2+} in ZNTFH is a Jahn-Teller ion,[13] while the Cu^{2+} ion in CCDAH is a non-Jahn-Teller ion. If the impurity ion exhibits a Jahn-Teller effect then the effect can bring about an additional change in soft mode frequency [different from that in (i) above], and thus can modify the phase-transition behavior of the host lattice significantly from that without the impurity.[12–15] The change in soft mode frequency can change T_c as explained earlier.[10]

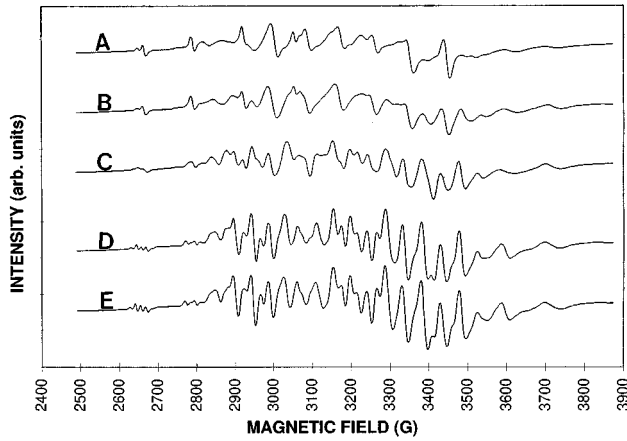To obtain more experimental data on the modification of

FIG. 1. EPR spectra of $Cd_{1-x'}Mn_{x'}(CH_3COO)_4 \cdot 6H_2O$ with x' $= 0.249\%$, at temperatures above and below the phase transition (using a very small amount of $Cu^{2+} \sim 0.008\%$). The temperatures at which the spectra were taken are $A = 125$ K, $B = 120$ K, $C = 115$ K, $D = 60$ K, $E = 50$ K.

the structural phase-transition temperature of CCDAH as a function of concentration of different paramagnetic impurity ions, we grew CCDAH crystals with different Mn^{2+} ion concentrations and identified the temperature of the phase change in these crystals by EPR. The observed modifications in phase transition of CCDAH with Mn^{2+} impurities are compared with those induced by Cu^{2+} impurities. This study provides more experimental data on the role of impurity mass on the modifications of phase transition of the host lattice CCDAH, and from this and the previous[10] data we identify the soft mode responsible for the phase transition in CCDAH.

II. EXPERIMENTAL DETAILS

Single crystals of CCDAH were grown by slow evaporation at room temperature from aqueous solutions containing equal molar amounts of cadmium acetate and calcium acetate by weight. Known amounts of manganese acetate were added to give crystals with different concentrations of Mn^{2+} ions. A very small but fixed amount of copper acetate was added to each solution, so that the Cu^{2+} ion could be used as a probe to study the phase transition of the crystal by EPR. (The resolution of the copper hyperfine lines at orientations of the magnetic field near the c axis made the Cu^{2+} ion a better probe than the Mn^{2+} ion to detect phase transition in the crystals investigated.) The crystals grew with an elongated habit along the c axis. Axes, a' and b', perpendicular to the c axis and the well-defined faces described by Eachus *et al.*[16] were used to identify the EPR spectra. An APD Cryogenics HC-4 closed-cycle refrigerator was used to vary the temperature of the sample in the EPR cavity in the temperature range 20–300 K. The temperature could be controlled to ± 0.5 K and the accuracy of the reported transition temperatures is ± 1 K. The EPR spectra were taken with a Varian E-Century Line spectrometer operating at 9.3 GHz. The percentage weights of Cu^{2+} and Mn^{2+} in one of the samples was determined accurately (2.5%) by Galbraith Laboratories, Inc., Knoxville, TN. The percent weights of Cu^{2+} and Mn^{2+} in other samples were determined (with an

accuracy of about 5%) by comparison of the intensities of EPR hyperfine transitions corresponding to $m_I = -1/2$ and $m_I = -5/2$ for Cu^{2+} and Mn^{2+}, respectively, with those of the analyzed sample.

Each crystal was oriented with the c axis about 20° from the external magnetic field. In this orientation, the intensity of the EPR spectrum due to the small amount of Cu^{2+} ion is appreciable at temperatures above T_c. T_c was determined by recording EPR spectra at different temperatures and noting the temperature at which there was a substantial decrease in the intensity and the onset of splitting of the Cu^{2+} spectra (Fig. 1).

III. RESULTS AND DISCUSSION

The experimental phase-transition temperature, T_c of $CaCd_{1-x}Mn_x(CH_3COO)_4 \cdot 6H_2O$ as a function of effective Mn^{2+} concentration is shown in Fig. 2 as well as in Table I. The effective atomic fraction, x', of Mn^{2+} in $CaCd_{1-x}Mn_yCu_z(CH_3COO)_4 \cdot 6H_2O$ ($z \ll y$ and $x = y + z$), is calculated as follows:

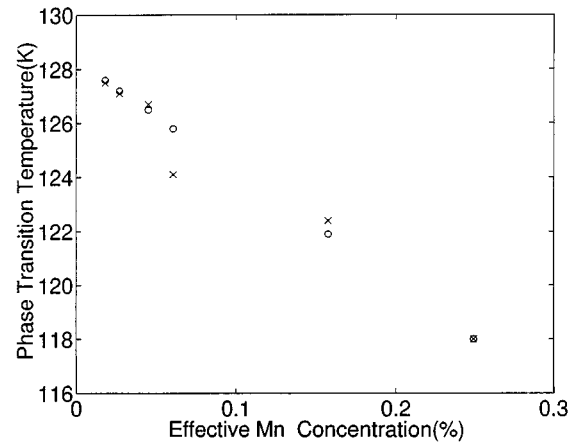$$x' = y + zA_{Cu}/A_{Mn}, \qquad (1)$$

FIG. 2. Phase transition temperatures in CCDAH as a function of effective atomic fraction of manganese ion concentrations. $\times$ indicates measured values and $\bigcirc$ indicates computed values.

TABLE I. Experimental and theoretically computed values of the phase-transition temperature of $CaCd_{1-x}Mn_x(CH_3COO)_4 \cdot 6H_2O$ as a function of x'.

Effective atomic fraction of Mn^{2+} x' (%)	$T_{c(obs)}$ (K) ± 1	$T_{c(cal)}$ (K) with $T_{co}(Mn^{2+}) = 128.4$ K
0.249[a]	118	118
0.1585	122.4	121.9
0.0605	124.1	125.8
0.0452	126.7	126.5
0.0272	127.1	127.2
0.0182	127.5	127.6

[a]The matching point with theory.

TABLE II. Experimental and theoretically computed values of the phase-trasition temperature of $CaCd_{1-x}Cu_x(CH_3COO)_4 \cdot 6H_2O$ as a function of x.

Percentage weight of copper (II) ions	Corresponding x	Expt. T_c[a] ± 1 K	Computed T_c (K)
0.1	0.0078	143.5	143.4
0.2	0.0156	142.0	141.8
0.3	0.0234	140.5	140.1
0.4	0.0312	139.0	138.5
0.5	0.0389	137.6	136.8
0.6	0.0467	136.0	135.2
0.7	0.0544	134.6	133.5
0.8	0.0621	133.1	131.9
0.9	0.0698	131.6	130.2
1.0	0.0775	130.1	128.5
1.1	0.0852	128.6	126.8
1.2	0.0929	127.1	125.1
1.3	0.1006	125.6	123.3
1.4	0.1082	124.1	121.6

[a]The experimental values are taken from the straight-line fit of the observed data as reported in Fig. 2 of Ref. 10.

where A represents the atomic mass. The calculated x' is slightly higher than $y+z$. The experimental T_c of $CaCd_{1-x}Cu_x(CH_3COO)_4 \cdot 6H_2O$ as a function of x as obtained from our previous study[10] is shown in Table II. The relation between x and percent weight w is shown later. It can then be easily seen from Tables I and II that $-\Delta T_c/\Delta x$ is significantly higher for the effective atomic fraction of Mn^{2+} ions than it is for only Cu^{2+} ions in CCDAH. From Table I, we find that the limiting value of $T_{co}(Mn^{2+})$, when the effective atomic fraction of Mn^{2+} ions goes to zero, is about 128.4 K. This is strikingly different from 145 K for $T_{co}(Cu^{2+})$.[10] Below, we explain theoretically the dependence of T_c on x and x' for the two different types of paramagnetic impurity ions in $CaCd_{1-x}M_x(CH_3COO)_4 \cdot 6H_2O$ ($M = Cu^{2+}$ or Mn^{2+}) and the absence of a phase transition in $CaCu(CH_3COO)_4 \cdot 6H_2O$.

In the mean-field theory of soft modes, the square of the frequency of the optic mode which freezes out at the phase transition[17,18] is

$$\omega^2 = K(T - T_c), \qquad (2)$$

where K is a constant and T_c is the temperature of the phase transition. As pointed out in an earlier paper,[10] the change in phase-transition temperature with Cu^{2+} ion concentration in the crystal can be linked with an increase of the soft mode frequency when the heavier cadmium ion is replaced by the lighter copper ion.

Let T_{co} and T_c be the transition temperatures when the impurity concentration is zero (i.e, $x=0$) and when the impurity concentration corresponds to the atomic fraction x. $T_{co}(Cu^{2+}) = 145$ K.[10] In the present study, as mentioned earlier, Mn^{2+} ions are introduced in CCDAH to affect the transition temperature while a very small amount of Cu^{2+} ion is used for precise determination of T_c. Also let $\Delta T_c = T_{co} - T_c$, then

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

or

$$\omega^2/\omega_0^2 = 1 + K\Delta T_c/\omega_0^2, \qquad (3)$$

where ω_0 is the soft mode frequency of the pure lattice (i.e., without impurity). Let us focus our attention on what happens to ω as the sample is doped with various amount of Cu^{2+} ions, at a temperature where $T = T_{co} - \delta$, with $\delta \ll T_{co}(\sim 1 \, ^\circ C)$. At this temperature ($T = T_{co} - \delta$), ω_0 of pure CCDAH is still finite. For the doped crystal, we shall write $\omega_{0\delta}$ for ω_0 and ω_δ for ω. Here, it is to be noted that both the doped crystal and the pure crystal (i.e., CCDAH) have the same crystal structure (since low concentrations of the dopant are used).

Then from Eq. (2), we get at a temperature $T = T_{co} - \delta$,

$$\omega_\delta^2/\omega_{0\delta}^2 = 1 + K\Delta T_c/\omega_{0\delta}^2. \qquad (4)$$

As mentioned before, the metal ions at $T > T_c$ lie in a chain along the c axis, while below T_c they are believed to have a zigzag pattern along the c axis leading to an orthorhombic distortion. Therefore, we may assume to a reasonable approximation that the soft mode frequency, ω, which goes to zero at T_c corresponds to one of the natural modes of harmonic vibration of the -Ca-$Cd_{1-x}Cu_x$-Ca- chain along the c axis in this crystal. Substituting an impurity paramagnetic ion for the cadmium ion changes the vibrational mode frequency of the chain. This should be thought of as a small perturbation in the mode frequencies. We assume that this small perturbation does not change K in Eq. (2), or the spring constant C of the harmonic lattice as the structure of both doped and undoped crystals are assumed to be the same. For the soft optic mode of the diatomic chain, at $T = T_{co} - \delta$,

$$\omega_0^2 = 2C(m + m_{ca})/mm_{Ca}, \qquad (5)$$

where m_{ca} represents the mass of the Ca atom and m represents the mass of the $Cd_{1-x}M_x$ combination (M = impurity atom). Here, $m = (1-x)m_{cd} + xmi$, and when $x=0$, $\omega = \omega_{0\delta}$.

Assuming the spring constant C does not change significantly for low values of x, it can be shown that

$$\omega_\delta^2/\omega_{0\delta}^2 - 1 = x(a-b)/(1-ax), \qquad (6)$$

and using Eq. (4) that

$$K\Delta T_c/\omega_{0\delta}^2 = x(a-b)/(1+bx), \qquad (7)$$

where

$$a = (M_i - M_{Cd})/(M_{ca} + M_{Cd}), \quad b = (M_i - M_{Cd})/M_{Cd}. \qquad (8)$$

Here, M represents the atomic mass of the atom or ion concerned. M_i is the atomic mass of the impurity ion.

Equation (7) should quantify the change of transition temperature of a harmonic lattice with small amounts of impurities (so that the strains created by the impurities would not be significant). Using Eq. (7), $K/\omega_{0\delta}^2$ can be obtained by measuring ΔT_c for a given x. The value of $K/\omega_{0\delta}^2$ so obtained can then be used in Eq. (7) to compute ΔT_c for different values of x in $CaCd_{1-x}M_x(CH_3COO)_4 \cdot 6H_2O$.

For the case of Cu^{2+} impurity in CCDAH we take the experimental value of ΔT_c for a Cu^{2+} concentration of 1.32% by weight as in Ref. 10. The following equation is used to obtain x from the percentage weight (w):

$$x = 4.9648w/(63.5 + 0.489w). \quad (9)$$

It should be noted that the % wt from the chemical analysis of the crystal can be different from that of the solution from which the crystal is grown. In the case of the Mn^{2+} impurity in CCDAH,

$$x = 4.964w/(54.9 + 0.575w). \quad (10)$$

Using $a = -0.32087$ and $b = -0.43505$ from Eq. (8), we then obtained $K/\omega_{0\delta}^2$ for Cu^{2+} in CCDAH, using Eq. (7). The calculated value of $K/\omega_{0\delta}^2$ is 554.7×10^{-6} K^{-1}. This value of $K/\omega_{0\delta}^2$ is used to compute ΔT_c and hence the transition temperature, T_c(th) with the same equation, for different values of x. The computed values are given with the experimental values[10] in Table II. The agreement between the experimental values of T_c and the computed values of T_c in CCDAH for the different Cu^{2+} concentrations is quite good for small concentrations. For higher Cu^{2+} impurity concentration, the maximum difference between the computed T_c and experimental T_c is about 2.5 °C. The maximum error in experimental T_c in Ref. 10 is ± 1 °C. This good agreement between experiment and theory, especially at the low concentration of Cu^{2+}, supports the assumption that the soft mode frequency which goes to zero at T_c in the CCDAH crystal is a vibrational mode of the Ca-$Cd_{1-x}Cu_x$-Ca- chain along the c axis. At high Cu^{2+} concentrations strains may cause a change in the spring constant C and additional change in T_c. Thus, the mean-field theory of the phase transition gives a good description of the experimental data, especially for copper impurities at small concentrations. Further investigation of the slight deviation of the computed T_c from experimentally observed T_c for a higher concentration is being carried out. It may be that for higher Cu^{2+} impurity concentrations, the nature of the phase transition deviates from that described by Landau's mean-field theory, since the critical exponent (which is 0.5 for mean-field theory), may vary with Cu^{2+} concentration.[10,12] In such a case, Eq. (2) may be described by

$$\omega^2 = K(T - T_c)^r, \quad (11)$$

with $r/2 =$ critical exponent and $r < 1$. Table II shows that the observed T_c is somewhat higher than the T_c computed from the mean-field theory for high Cu^{2+} concentration, i.e., above 1% (percentage weight). The critical exponent was not determined as a function of Cu^{2+} concentration, but it appears that $r/2 < 0.5$ in Eq. (11) is consistent with the observation for high Cu^{2+} concentration.

Deviations from $r/2 = 0.5$ (mean-field theory) can be found near the critical point terminating a first-order phase boundary, where a second-order transition may occur.[19] Microscopically, this results from correlated fluctuations of the order parameter, whereas Landau's mean-field theory is correct for uncorrelated fluctuations with a Gaussian distribution.[19] The deviation from Landau theory becomes appreciable when the length of the correlated fluctuation

$\{\xi(T - T_c)^{-1/2}\}$ exceeds the range λ of the forces. With very low impurity concentration, λ of the forces giving rise to the collective excitation of the lattice may be much larger than ξ and deviation from $r/2 = 0.5$ can occur in a very small temperature range, which is so close to T_c that no deviation can experimentally be detected. Whereas with high impurity concentration, collective excitation may be impeded by local modes of vibrations around the impurity ions, and ξ increases and may even exceed λ. Then the deviation from $r/2 = 0.5$ can occur appreciably far from T_c, and $r/2 < 0.5$ can be experimentally detected for high impurity concentration. To further elucidate this theory, determinations of the critical exponents should be made for CCDAH at high and low Cu^{2+} concentrations.

The phase-transition temperature in CCDAH with Mn^{2+} impurities may also be calculated from Eq. (7). As before, $\Delta T_c = T_{co}(Mn^{2+}) - T_c$. For Mn^{2+} in CCDAH, $a = -0.37683$ and $b = -0.51120$. When the value of $K/\omega_{0\delta}^2$ obtained for Cu^{2+} ions is used in Eq. (7) to compute ΔT_c and hence T_c of CCDAH as a function of the effective atomic fraction of Mn^{2+} ions, x', we find that the agreement between the observed and computed values is poor. The experimental observations are better explained if the value of $K/\omega_{0\delta}^2$ is determined separately by using the observed value of $\Delta T_c (= 10.4$ K) for Mn^{2+} ions (effective atomic fraction $x' = 0.00249$). This is found to be $= 3.22 \times 10^{-5}$ K^{-1}. With this value of $K/\omega_{0\delta}^2$, ΔT_c and hence T_c are computed for other concentrations of Mn^{2+} ions. These values as shown in Table I are in good agreement with the experimental values.

Though the simple theory presented above explains very well our observed transition temperatures in CCDAH as a function of the atomic fraction of impurities, two observations are noteworthy.

(1) The value of $T_{co}(Mn^{2+})$ is 128.4 K and this is significantly different from 145 K determined for $T_{co}(Cu^{2+})$ in our earlier paper.[10] We have rechecked the APD temperature controller system by measuring T_c with a known value of copper concentration (without manganese), and reconfirmed $T_{co}(Cu^{2+})$.[10] It may be mentioned that Sikdar and Pal[11] indicated a possible second phase transition at ~ 128 K in CCDAH, which we could not establish convincingly in our previous study, using only the Cu^{2+} probe.[10] It is possible that Mn^{2+} and Cu^{2+} ions couple differently with two soft modes which are responsible for phase transition in CCDAH at 128 and 145 K (when $x \to 0$), respectively. The difference between T_{co} for Cu^{2+} and Mn^{2+} impurities is hard to explain, and more studies on phase transitions of CCDAH using other types of paramagnetic impurities may be necessary to unravel this. It may be mentioned that the orbital ground states, for ^6S Mn^{2+}, and for ^2D Cu^{2+} are different in the tetragonally distorted octahedral environment of H_2O ligands in CCDAH crystals. This might also suggest that Mn^{2+} and Cu^{2+} may couple differently with the soft modes of the crystal.

(2) The value of $K/\omega_{o\delta}^2$ obtained from studies of Mn^{2+}-doped crystals is significantly different from that of Cu^{2+} doped crystals. From the above theory, $-dT_c/dx$ for a given ion is proportional to $\omega_{o\delta}^2/K$ at low concentrations and the observations indicate that $-dT_c/dx$ for Mn^{2+} ions is significantly higher than that for Cu^{2+} ions. It may be argued

that $\omega_{o\delta}$ should be independent of the nature of the impurity ions, but this does not rigidly hold for the mean-field constant K.

Only EPR has been used to study the phase transition in CCDAH, but in several other studies EPR and other techniques have been used to determine phase transition in the same material. Some of the materials studied and the other techniques used are BaTiO$_3$ (electric polarization),[19–22] CaBa(C$_2$H$_5$COO)$_6$ (dielectric),[23–25] N(CH$_3$)$_2$CoCl$_4$ (dielectric),[26–28] Rb$_2$ZnCl$_4$ (dielectric),[29] ZnTiF$_6$·6H$_2$O (NMR, infrared),[30–32] and Cd$_2$(NH$_4$)$_2$(SO$_4$)$_2$ (dielectric, Raman spectroscopy).[33–35] For CaBa(C$_2$H$_5$COO)$_6$, a material similar to CCDAH, dielectric studies of the room-temperature cubic crystal (phase I) shows that it undergoes a transition at 267 K (first order), and another transition near 198 K (second order). Single-crystal and powder EPR studies of this material show (i) a doubling of the spectra from the inequivalent sites and a sharp change in the magnitude as well as the orientation of the zero-field tensor across the 267-K transition; and (ii) and the inflection point in the plot of the value of the zero-field tensor versus T across the 198 K transition. In all of the above materials there is good agreement between the phase temperatures determined with EPR and the other techniques.

In Eq. (7) above, if we use $x=1$ then ΔT_c should clearly correspond to that of CaCu(CH$_3$COO)$_4$·6H$_2$O, and a phase-transition temperature of $T_c=-219$ K is predicted, using the value of $K/\omega_{o\delta}^2$ obtained above for the Cu^{2+} impurity in CCDAH. Indeed, no phase transition has been observed in CaCu(CH$_3$COO)$_4$·6H$_2$O, though this crystal has been extensively studied by a host of workers.[9] This lends additional support to the theory presented above.

IV. SUMMARY

The phase-transition temperature of single crystals of CaCd$_{1-x}$Mn$_x$(CH$_3$COO)$_4$·6H$_2$O as a function of x, has been studied using a very small amount of copper as an EPR probe. The rate of lowering of T_c with x i.e., $-dT_c/dx$ is much larger for the Mn^{2+} impurity in calcium cadmium acetate hexahydrate than it is for only Cu^{2+} (Ref. 10) and the limiting value of T_{co}(Mn^{2+}) as the Mn^{2+} ion concentration tends to zero is significantly lower than that of T_{co}(Cu^{2+}). Mean-field theory and harmonic vibration of the -Ca-Cd$_{1-x}$-Cu$_x$-Ca- chain along the c axis of the crystal explains the lowering of the phase transition temperature in CaCd$_{1-x}$Cu$_x$(CH$_3$COO)$_4$·6H$_2$O as x increases. The simple theory also explains the absence of a phase transition in CACu(CH$_3$COO)$_4$·6H$_2$O.

The observed lowering of the phase-transition temperature in CaCd$_{1-x}$Mn$_x$(CH$_3$COO)$_4$·6H$_2$O as x increases can be explained very well by this theory, but it requires a value of $\omega_{o\delta}^2/K$ which is significantly different from that of CaCd$_{1-x}$Cu$_x$(CH$_3$COO)$_4$·6H$_2$O. This higher value of $\omega_{o\delta}^2/K$ is consistent with the significantly higher value of the observed $-dT_c/dx$ for CaCd$_{1-x}$Mn$_x$(CH$_3$COO)$_4$·6H$_2$O. Further experiments using different types of paramagnetic impurities in crystals of CCDAH may help one to understand why T_{co}(Cu^{2+}) and $\omega_{o\delta}^2/K$(Cu^{2+}) are significantly different from T_{co}(Mn^{2+}) and $\omega_{o\delta}^2/K$(Mn^{2+}). Progress is being made to refine the theory presented above by taking into consideration the change of the spring constant C with impurity concentration.

With the above simple theory, it will be possible to compute ΔT_c in other systems, such as ZnTiF$_6$·6H$_2$O (Ref. 12) for various concentrations of Ni^{2+} and Cu^{2+} ions doped in ZnTiF$_6$·6H$_2$O. The contribution of the Jahn-Teller effect to ΔT_c in ZnTiF$_6$·6H$_2$O (Ref. 12) due to the presence of Cu^{2+} could be evaluated. Work on this will be reported later.

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