EPR studies of the effect of Zn^{2+} ion impurities in phase transition of $CaCd(CH_3COO)_4 \cdot 6H_2O$ crystals

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The effect of Zn^{2+} ion impurities on the phase transition temperature of single crystals of calcium cadmium acetate hexahydrate (CCDAH) has been studied using the electron-paramagnetic-resonance technique. The lowering of the phase transition temperature as a function of increasing Zn^{2+} impurity ion concentration in the crystals has been observed to be quite different from that found in our earlier studies of Cu^{2+} and Mn^{2+} ion doped crystals. Though the observed lowering of phase transition temperature with atomic fraction x of the Zn^{2+} impurity ion can be explained fairly well in terms of mean-field theory and a soft mode arising out of the harmonic vibration of the Ca-$Cd_{(1-x)}Zn_x$-Ca chain along the c axis of the crystal, contrary to expectation, values of constants (such as the ratio of the square of the soft-mode frequency before transition, the mean-field constant, and the phase transition temperature, etc. of the pure crystal) are quite different from that obtained by fitting the phase transition temperatures in the Cu^{2+} ion only impurity doped crystals. The temperature variation of the spin-Hamiltonian parameters of the Cu^{2+} ion probe in the Zn^{2+}-doped crystal of CCDAH is somewhat different from that in the Cu^{2+} ion only doped crystal. Deviation from mean-field theory is then considered in the Zn^{2+} impurity driven modification of phase transition of the crystal and good agreement between the observed and computed values of phase transition temperature as a function of the Zn^{2+} atomic fraction has been obtained using the same values of the said constants as obtained for Cu^{2+} ion only impurity doped crystals.

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I. INTRODUCTION

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, $CaCu(CH_3COO)_4 \cdot 6H_2O$ (CCUAH).[1] Both have tetragonal symmetry belonging to the space group $I4/m$. In the CCDAH lattice the Cd^{2+} ion is surrounded by eight oxygen atoms in a slightly distorted dodecahedral configuration characterized by D_{2d} symmetry. The Ca^{2+} ion, on the other hand, is coordinated with six oxygen ions occupying a C_{2h} site symmetry (approximately D_2 symmetry). The latter crystal (i.e., CCUAH), which has been studied by a good number of workers, does not exhibit any structural phase transition within the temperature range 350–1.2 K.[1] By comparing the structures of CCUAH and CCDAH containing a Cu^{2+} ion, Mabbs and Smail[2] concluded that the Cu^{2+} ion substitutes for a Cd^{2+} ion in CCDAH. Zhou[3] calculated the crystal-field energy splittings and Zeeman g factors of a Cu^{2+} ion under both D_{2d} (Cu^{2+}) and C_{2h} (Ca^{2+}) symmetries in CCDAH. Calculated and observed values agree for D_{2d} (Cu^{2+}) symmetry (i.e., when a Cu^{2+} ion replaces a Cu^{2+} ion in CCDAH). Several electron-paramagnetic-resonance (EPR) studies[4–7] also confirm that the Cu^{2+} ion substitutes for Cd^{2+}.

Replacement of copper by the larger cadmium ion in CCUAH introduces phase transition in this crystal.[6] Using the EPR of Cu^{2+} as a probe, the phase transition temperature T_c of $CaCd_{1-x}Cu_x(CH_3COO)_4 \cdot 6H_2O$ is found to vary 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+}.[5] The phase transition temperature of pure CCDAH (i.e., $x=0$), T_{co}, was deduced from this study to be 145 K.[5]

To shed some light on the modification of phase transition temperature of CCDAH by impurities, Oguama, Shields, and De[8] carried out detailed EPR studies of phase transition in CCDAH doped with Mn^{2+} ions of various atomic concentrations, x. They found that $-dT_c/dx$ for Mn^{2+} is much higher than that for Cu^{2+}. They also noticed that the value of T_{co} obtained by using a Mn^{2+} ion probe [abbreviated as $T_{co}(Mn^{2+})$], 128.4 K, is significantly different from the phase-transition temperature $T_{co}(Cu^{2+})$, 145 K obtained by using a Cu^{2+} ion probe.[5] The changes in T_c from 143 to 122 K as a function of Cu^{2+} ion concentration in CCDAH is explained[8] in terms of mean-field theory together with a vibrational mode of the Ca-$Cd_{1-x}A_x$-Ca chain along the c axis of the crystal, where A stands for the impurity atom. Our findings also support the fact that Cu^{2+} replaces the Cd^{2+} ion in CCDAH.[2,3,7] Contrary to the observation of Chand and Upreti[7] and Jain, Saraswat, and Upreti[6] that Mn^{2+} replaces the Ca^{2+} ion in this crystal, our observation[8] of the effect of Mn^{2+} ion concentration on phase transition of CCDAH crystals can only be explained by assuming that the Mn^{2+} ion replaces a Cd^{2+} ion, not a Ca^{2+} ion in the crystal. However, a value of $\mathbf{K}/\omega_{0\delta}{}^2$ of 3.22×10^{-5} K^{-1} was required.[8] Here $\mathbf{K}$ is the mean-field constant and $\omega_{0\delta}$ is the soft-mode frequency of the pure lattice immediately before the phase transition occurs. This is far smaller than the value of 55.4×10^{-4} K^{-1} found using a Cu^{2+} ion probe in CCDAH. Also, the value for T_{co} of 128.4 K obtained using a Mn^{2+} ion probe was found to be quite different from that of 145 K

TABLE I. Experimental and theoretically computed values of the phase-transition temperatures of $CaCd_{1-x}Zn_x(CH_3COO)_4 \cdot 6H_2O$ as a function of x assuming mean-field theory of phase transition. For the theoretically computed values, $\omega_{0\delta}{}^2/\mathbf{K}=16\,109$ K and $T_{co}=140$ K (see text) were used.

Atomic fraction[a] of Zn^{2+}	Atomic fraction[a] of Cu^{2+}	Effective atomic fraction of Zn^{2+}	$T_{c(\mathrm{obs})}$ (K) ± 1	$T_{c(\mathrm{cal})}$ (K) ± 1.3
0.0205	0.0002	0.0207	103	103
0.0182	0.0002	0.0184	107	107.1
0.0140	0.0002	0.0142	119	115
0.0034	0.0008	0.0042	129	132.7
0.0018	0.0007	0.0025	134	135.5

[a]As determined by Galbraith Laboratories Inc., TN. Accuracy is ± 0.0001.

obtained using a Cu^{2+} ion probe. A reason for this interesting result was suggested in our earlier paper[8] in which Mn^{2+} and Cu^{2+} was found to possibly be coupling differently with the soft modes of the crystal. This suggestion seems to be corroborated by the earlier findings of Chand and Upreti.[7] From their EPR studies of CCDAH using a Mn^{2+} ion probe they found a second-order phase transition at 128 K, when the large amplitude hindered motion of the CH_3 becomes frozen.

To obtain more experimental data on the modification of the structural phase transition of CCDAH by impurities, to understand the coupling mechanism of the impurities with the two soft modes of the crystal, and thus to gain a deeper understanding of the role of impurity dynamics in phase transition of crystalline solids in general, we grew CCDAH crystals with different Zn^{2+} ion concentrations and identified the temperature of the phase change in these crystals by using a trace amount of a Cu^{2+} ion as a probe. This study provides experimental data on the role of the Zn^{2+} ion in CCDAH. An analysis of the data shows a deviation from the mean-field theory in phase transition of CCDAH and suggests a possibility of coupling of the Zn^{2+} ion with the two soft modes in the crystal.

II. EXPERIMENTAL DETAILS

Single crystals of CCDAH were grown at room temperature by slow evaporation of aqueous solutions containing equal molar amounts of cadmium acetate and calcium acetate by weight. Known amounts of zinc acetate were added to give crystals with different concentrations of Zn^{2+} ions. The ratios of the Zn^{2+} ion to Cd^{2+} ions in the five solutions were 1:10, 1:20, 1:50, 1:100, and 1:400. 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 Cu^{2+} hyperfine lines at orientations near the c axis made the Cu^{2+} ion an excellent probe to detect phase transition in the crystal investigated.) The crystals grew with the elongated habit along the c axis. Axes a' and b', perpendicular to the c axis, and the well-defined faces described by Eachus, Herring, and Phol[9] were used to record the EPR spectra using the methods described in Ref. 8. As the sample is cooled at a uniform rate of 1 °C per 15 min, the intensity of the Cu^{2+} hyperfine lines increased substantially except in the neighborhood of T_c, where a reduction in the EPR signal intensity was observed and T_c was noted as the temperature at which a substantial decrease in the intensity was first observed. This was followed by the onset of the line splitting. At a temperature appreciably below T_c, the spectral features resemble that of the Cu only doped CCDAH, as reported in Ref. 5. Percentage weights of the Zn^{2+} ions in the crystals (that were investigated) were analyzed by Galbraith Laboratories, Inc., Knoxville, TN. The percentage weight of the Cu^{2+} ion in one sample was determined by the same laboratory. The percentage weights of the Cu^{2+} probes in other samples were determined from the comparison of intensities of Cu^{2+} EPR hyperfine transitions at 200 K. The corresponding atomic fractions are given in Table I.

III. RESULTS

The experimental phase transition temperature T_c of $CaCd_{1-x}Zn_x(CH_3COO)_4 \cdot 6H_2O$ single crystals as a function of x is shown in Table I. The values of x in Table I were calculated from the percentage weight (w) of Zn^{2+}, using the following relations:

$$x = 4.964w/(65.37 + 0.470w). \tag{1}$$

The effective atomic fraction x' can be calculated from the following relation:

$$x' = x + yM_{\mathrm{Cu}}/M_{\mathrm{Zn}},$$

where M represents the atomic mass and y is the atomic fraction of Cu^{2+} in the sample. Table I above, together with Tables I and II of Ref. 8 show that $-dT_c/dx$ is significantly higher for Mn^{2+} than it is for Zn^{2+} and Cu^{2+} ions and that $-dT_c/dx$ for Zn^{2+} ions is much higher than that for Cu^{2+} ions in CCDAH Ca-$Cd_{1-x}Cu_x$-Ca along the c axis in the CCDAH crystal.

Substituting the impurity ion for cadmium changes the soft-mode frequency[10,11] of the crystal and this brings about a change[5,8] in T_c. Assuming that the soft-mode frequency obeys mean-field theory[10,11] it was shown in Ref. 8 that

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

where

$$a = (M_1 - M_{\mathrm{Cd}})/(M_{\mathrm{Ca}} + M_{\mathrm{Cd}}),$$

$$b = (M_1 - M_{\mathrm{Cd}})/M_{\mathrm{Cd}},$$

and

$$\Delta T_c = T_{co} - T_c . \quad (3)$$

Using Eq. (1), the best fit values of T_c for the different effective atomic fractions x' of the Zn^{2+} ion in CCDAH are obtained for $T_{co} = 140$ K and $\omega_{0\delta^2}/\mathbf{K} = 16\,109$ K. These are shown in Table I.

IV. DISCUSSION

Our studies on the modification of phase transition with impurities in CCDAH reveal that the rate of change of transition temperature T_c with the impurity atomic fraction x depends on the nature of the impurity. We see from Table I and Tables I and II of Ref. 11 that for each of the three different types of impurities, the variation of T_c in CCDAH crystals with x can be explained fairly well in terms of mean-field theory and a soft vibrational mode of the linear chain Ca-$Cd_{1-x}A_x$-Ca along the c axis of the crystal. However, this theory, which is also successful in explaining the absence of phase transition in $CaCu(CH_3COO)_4 \cdot 6H_2O$, requires different values of T_{co} and $\omega_{0\delta^2}/\mathbf{K}$ for the three types of impurities (see Table I and Ref. 8). The ionic radii of Cu^{2+} and Zn^{2+} are nearly the same, viz., 0.74 and 0.72 Å. If mean-field theory governs the phase transition in both cases, then these two ions are not expected to modify the phase-transition temperature in CCDAH in a widely different way as observed in our present investigation. In other words, the values of $\omega_{0\delta^2}/\mathbf{K}$ should have been found to be nearly the same for the two ions.

To see if the observed changes in T_c with Zn^{2+} impurity ion concentration in CCDAH could be explained with the same values of T_{co} and $\omega_{0\delta^2}/\mathbf{K}$ as obtained for CCDAH crystals doped with the Cu^{2+} impurity ion, we considered the possibility of a deviation from mean-field theory for the phase transition of Zn^{2+}-doped CCDAH. In such a case the square of the frequency of the soft mode that freezes out at phase transition may be given by

$$\omega^2 = \mathbf{K}(T - T_c)^r, \quad (4)$$

where $r/2$ is the critical exponent with $r < 1$. Such deviations can be found near the critical point terminating a first-order phase boundary, where a second-order transition may occur.[12]

Now, considering the soft optic mode of vibration of the Ca-$Cd_{1-x}Zn_x$-Ca chain along the c axis and following the arguments behind Eqs. (3)–(8) of Ref. 8, it can be shown that the changes in transition temperature with impurity concentration in CCDAH are given by

$$\Delta T_c = (\omega_{0\delta^2}/\mathbf{K})^{1/r}[\{1 + x(a-b)/(1+bx)\}^{1/r} - 1], \quad (5)$$

where a and b are given by Eq. (3). It is to be noted that Eq. (2) is a special case of Eq. (5) when $r = 1$.

The values of T_c computed for Zn^{2+}-doped CCDAH using Eq. (5) and the same values of T_{co} and $\omega_{0\delta^2}/\mathbf{K}$ as obtained for those of Cu^{2+}-doped CCDAH (Ref. 8) are given in Table II, for $r = 0.783 \pm 0.005$. From Table II it is seen that though the agreement between the computed values of T_c and the observed values of T_c is quite good for higher atomic fractions x', the agreement is not so good for lower atomic fractions. However, if we allow a small variation of r with concentration x, excellent agreement between the observed values of T_c and those of calculated T_c can be obtained (see Table II). The critical exponent r has been found to depend on impurity concentration.[13] The success of this model over that of the previous one (see Table I) lies in its ability to explain the observed variation of T_c with x for the same values of $\omega_{0\delta^2}/\mathbf{K}$ as obtained for Cu^{2+}-doped crystals.

TABLE II. Theoretically computed values of the phase transition temperature of $CaCd_{1-x}Zn_x(CH_3COO)_4 \cdot 6H_2O$ as a function of x, considering the possibility of deviation from mean-field theory and using the same values of $\omega_{0\delta^2}/\mathbf{K} = 1802.7$ K as obtained for Cu^{2+} only doped CCDAH (Ref. 11) and $r = 0.783$. For the values in parentheses, $r = 0.735$.

Effective atomic fraction of Zn^{2+}	$T_{c(\mathrm{obs})}$ ± 1 K	$T_{c(\mathrm{cal})}$ ± 1 K[b] for $r = 0.783$	$T_{c(\mathrm{cal})}$[a] ± 1 K[b]
0.0207	103	102.8	102.8 (0.783)
0.0184	107	107.5	107.5 (0.783)
0.0142	119	116.3	118.7 (0.790)
0.0042	129	136.7	129.3 (0.740)
0.0025	134	139.9	134.0 (0.730)

[a] T_c is calculated by allowing r to vary. The corresponding values of r are given in parentheses.

[b] The error in the fitted values of r is around ± 0.005.

In order to be able to throw some light on the link between the modification of phase transition and the change in local symmetry around the paramagnetic ion we also recorded the spin-Hamiltonian parameters ($g_\parallel, g_\perp, A_\parallel, A_\perp$) of the Cu^{2+} ion probe in a manner described earlier[8] in the temperature range 300–15 K. The temperature variations of the spin-Hamiltonian parameters and that of the normalized intensity I_N of one of its hyperfine transitions ($M_1 = \frac{3}{2}$) for one of the zinc-doped crystals ($x = 0.0034$) are shown in Figs. 1(a)–1(d).

The spin-Hamiltonian parameters (g and A tensors) remain tetragonal in the entire temperature range 300–15 K. Though the evidence of phase transition in the neighborhood of $T_c = 129$ K (see Table I for $x = 0.0034$) is discernible in the plots of $g_\parallel$ and I_N as a function of T [Figs. 1(a)–1(d)] the changes in the spin-Hamiltonian parameters ($g_\parallel$, $g_\perp$, and $A_\parallel$) are very small. Though the sharp change in the $g_\perp$ vs T plot [Fig. 1(b)] around 129 K indicates the presence of phase transition, it may be noted that the change is within experimental error ($\pm$ 0.002). Using Cu^{2+} EPR, the phase transition is best identified by observing the change in normalized intensity I_N. As the crystal is cooled from room temperature,

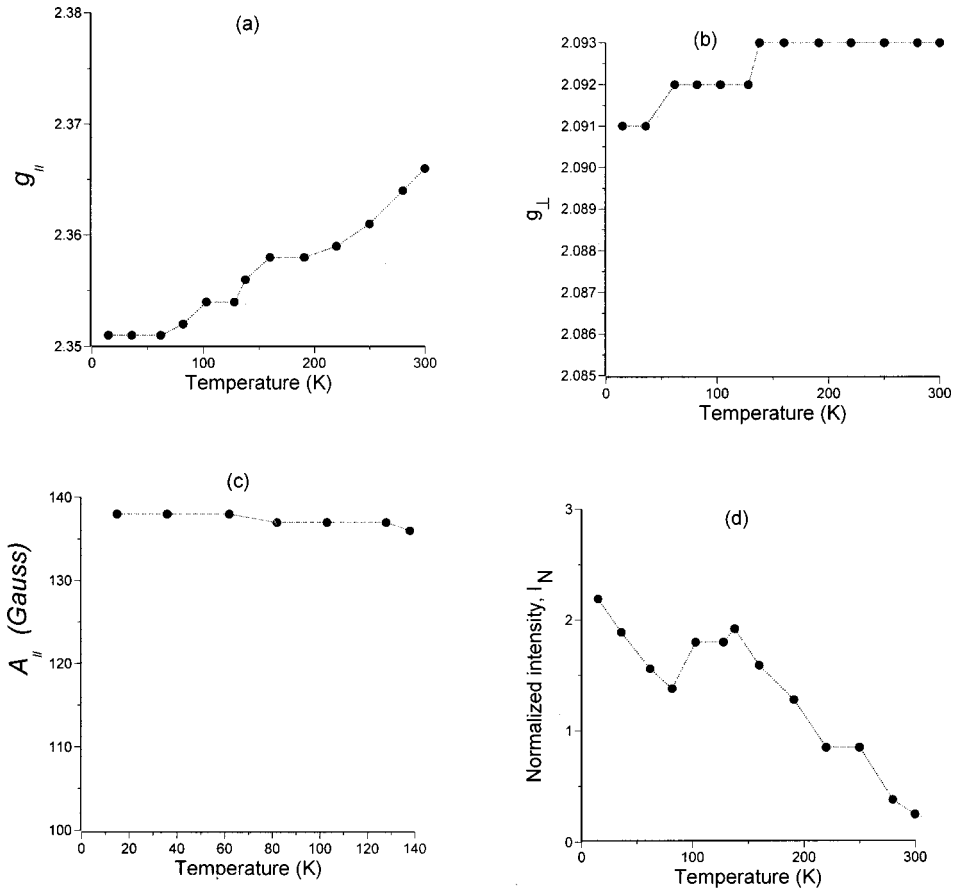

FIG. 1. (a) The temperature variation of $g_{\parallel}$ for the Cu^{2+} ion probe in $CaCd_{1-x}Zn_x(CH_3COO)_4 \cdot 6H_2O$ with $x=0.0034$. (b) The temperature variation of g_1 for the Cu^{2+} ion probe in $CaCd_{1-x}Zn_x(CH_3COO)_4 \cdot 6H_2O$ with $x=0.0034$. (c) The temperature variation of A_{11} for the Cu^{2+} ion probe in $CaCd_{1-x}Zn_x(CH_3COO)_4 \cdot 6H_2O$ with $x=0.0034$. (d) The temperature variation of normalized intensity I_N for the Cu^{2+} ion hyperfine line $(m_1=\frac{3}{2})$ probe in $CaCd_{1-x}Zn_x(CH_3COO)_4 \cdot 6H_2O$ with $x=0.0034$.

I_N continues to increase until the neighborhood of T_c is reached [Fig. 1(d)]. A significant decrease in I_N is then observed at T_c. I_N continues to increase as the crystal is cooled below T_c. The increase in I_N with lowering temperature is a usual feature in any EPR spectra of a Cu^{2+} ion and it is due to the increase in the population of the ground states as the higher states are depopulated. The decrease in I_N in CCDAH with lowering temperature in the neighborhood of T_c arises mainly from splitting the unit cells that contain ions, which are inequivalent below T_c.

The values of $g_{\parallel}$ of the Cu^{2+} ion in Zn^{2+}-doped CCDAH above the phase transition agree fairly well with that for the Cu^{2+} only doped crystal.[2,4] Whereas the $g_{\parallel}$ value for the Cu^{2+} crystal increased slightly below T_c, it decreases slightly in the case of the Zn^{2+}-doped crystal with lowering temperature. Though ^{63}Cu $A_{\parallel}$ increases slightly with lowering temperature in the Zn^{2+}-doped crystals, the values are almost the same as that for crystals predominantly doped with Cu^{2+} ions. The $g_{\parallel}$ and $A_{\parallel}$ values are found to be unaffected by the Zn^{2+} ion concentrations (within the range of concentrations used in this investigation). Considering the second-order perturbation and neglecting higher-order terms, the $g_{\parallel}$ and $g_{\perp}$ for the Cu^{2+} ion in a dodecahedral (D_{2d}) symmetry are given by

$$g_{\parallel}=2-8\lambda\alpha_{\parallel}/\Delta_{\parallel},$$

$$g_{\perp}=2-2\lambda\alpha_{\perp}/\Delta_{\perp},$$

where λ is the spin-orbit coupling constant (-829 cm^{-1}) for the ^2D Cu^{2+} ion, $\Delta_{\parallel}$ and $\Delta_{\perp}$ are the energy separation (due to the crystal-field splitting) of the states $^2B_2$ and ^2E from the ground $^2B_1$ state, and $\alpha_{\parallel}$ and $\alpha_{\perp}$ are the spin-orbit reduction factors. The above observation suggests that the variation of α/Δ with temperature is not similar for the crystal CCDAH doped separately with Cu^{2+} and Zn^{2+} ions. Whereas in the Cu^{2+} ion doped CCDAH $g_{\parallel}$, $A_{\parallel}$, $g_{\perp}$, and $A_{\perp}$ are found to be unaffected by Cu^{2+} concentrations, $g_{\perp}$ and $A_{\perp}$ in the case of the Zn^{2+}-doped CCDAH are found to depend slightly on the Zn^{2+} concentration. This may indicate the possibility that in the predominantly Zn^{2+}-doped crystal, the site symmetry around the metal ion and the antibonding orbitals (predominantly the metal orbitals) are not exactly the same as those in the Cu^{2+} ion, doped CCDAH crystals.

Then it is possible that the Zn^{2+} ion might have some coupling with the large amplitude hindered motion of the CH_3 group in CCDAH. Chand and Upreti[7] concluded from

the temperature variation of the linewidths of the Mn^{2+} that the large amplitude hindered motion (seen at room temperature) of the CH_3 becomes frozen at 128 K. Based on their result the said motion of the CH_3 group could be identified as the second soft mode of the CCDAH crystal. Their conclusion thus buttresses the suggestion made in our paper[8] (which was written without knowledge of Ref. 7) that Cu^{2+} and Mn^{2+} may couple differently with the soft modes of the crystal. It is then quite reasonable to conjecture that Mn^{2+} couples also to this second soft mode (particular attention should be paid to the fact that in the Mn^{2+}-doped crystal the phase transition temperature starts decreasing from 128 K as the Mn^{2+} ion concentration is increased,[8] rather than from 145 K when the Cu^{2+} ion concentration is increased in the Cu^{2+} only doped crystal). It was established that Cu^{2+} couples to the linear mode vibration of the chain axis. The deviation from mean-field theory that has been seen in the case of phase transition of Zn^{2+}-doped CCDAH may have its bearings on the Zn^{2+} ions coupling to these two soft modes in the crystal instead of just only to the vibrational mode of the linear-chain axis. This aspect and its influence on phase-transition behavior of impurity doped CCDAH as well as on the said temperature variation of the spin-Hamiltonian parameters need further investigation.

V. CONCLUSION

In the study of the phase transition of single crystals of $CaCd_{1-x}Zn_x(CH_3COO)_4 \cdot 6H_2O$ as a function of x, using Cu^{2+} as an EPR probe, it appears that there is a deviation from mean-field-type behavior in the Zn^{2+}-doped CCDAH. This could be due to coupling of the Zn^{2+} ion to more than one soft mode of the crystal viz., the linear vibration along the chain axis and one of the vibrational modes of the CH_3 group. Though the room-temperature values of $g_\parallel$, $g_\perp$, $A_\parallel$, and $A_\perp$ for the Cu^{2+} EPR probe in the Zn^{2+}-doped crystal are almost same as those of the Cu^{2+} only doped crystal, the temperature variations differ.

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