The phase transition temperature at 145 K in cadmium calcium acetate hexahydrate as a function of Cu$^{2+}$ probe concentration

H. Shields, T. G. Kleman, and D. K. De

Department of Physics, Wake Forest University, Winston-Salem, North Carolina 27109

(Received 17 March 1992; accepted 23 March 1992)

The temperature of the structural phase transition in cadmium calcium acetate hexahydrate as a function of Cu$^{2+}$ concentration has been studied with electron paramagnetic resonance (EPR). The phase transition temperature was found to vary from 144 to 124 K as the amount of copper varied from 0.07% to 1.3% of the sample weight. An extrapolation of this data predicts a structural phase transition at 145 K in pure cadmium calcium acetate hexahydrate. Good fits of the data to second-order phase transition theory was obtained with critical exponents close to 0.30.

I. INTRODUCTION

Cadmium calcium acetate hexahydrate, CaCd(CH$_3$COO)$_6$·6H$_2$O crystallizes from aqueous solution containing equal amounts of cadmium acetate and calcium acetate as large tetragonal prismatic crystals. Since the crystal structure of copper calcium acetate hexahydrate is isomorphous with that of cadmium calcium acetate hexahydrate, small amounts of copper may be incorporated in the cadmium calcium acetate hexahydrate crystal. Electron paramagnetic resonance (EPR) studies using copper as a paramagnetic probe in cadmium calcium acetate hexahydrate have given information on a structural phase change which occurs near 133 K. The metal ions at temperatures above the phase transition temperature lie along the $c$ axis of the crystal, while at temperatures below the phase transition they are believed to have a zig-zag pattern along the $c$ axis leading to an orthorhombic distortion.

A sudden splitting in the EPR spectrum at 133 K was observed and identified as a first-order phase transition by Sikdar and Pal. They observed a further splitting at 128 K which they attributed to a second-order transition. The reported phase transition temperatures range from 140 K in a sample containing ca. 0.5% copper to 128 K in a sample whose concentration was not specified. This large spread in transition temperature cannot be attributed to uncertainty in temperature measurements which are usually accurate to ±1 K. De$^6$ has demonstrated that the phase transition temperature in zinc fluoroitanate is strongly dependent on the Cu probe concentration. In this paper we have undertaken a detailed study of the phase transition of calcium cadmium acetate hexahydrate as a function of varying copper concentrations. We show that the phase transition temperature in cadmium calcium acetate depends on the concentration of the copper probe, and that the spread in reported phase transition temperatures lies within the range of phase transition temperatures we observed for different copper probe concentrations. We also show that the splitting reported by Sikdar and Pal at 128 K depends on the orientation of the crystal in the external field rather than a second independent phase change. The variation of our data for the splitting of the lowest field peaks as a function of temperature fits the description of a second-order phase change.

II. EXPERIMENTAL DETAILS

Single crystals of cadmium calcium acetate hexahydrate were grown by slow evaporation at room temperature from aqueous solutions containing equal molar amounts of cadmium acetate and calcium acetate with a small percent by weight of copper acetate. 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$^e$ et al. were used to identify the EPR spectra. An APD refrigerator was used to vary the temperature of a crystal in the EPR cavity. The temperature could be controlled to ±0.5 K and the accuracy of the reported temperatures is ±1 K. The EPR spectra studied were obtained with the direction of the magnetic field several degrees from the $c$ axis of the crystal. This is necessary because for temperatures above and below the phase transition temperature, the Cu$^{2+}$ ions are magnetically equivalent when the magnetic field lies along the $c$ axis, and the phase transition cannot be observed with EPR. The EPR spectra were taken with a Varian E–Century Line spectrometer operating at 9.1 GHz, and the percent weights of copper in the samples were determined by Galbraith Laboratories, Inc., Knoxville, TN.

III. RESULTS AND DISCUSSION

Typical EPR spectra of the Cu$^{2+}$ ion in cadmium calcium acetate hexahydrate are shown in Fig. 1. The phase transition temperature was taken as the temperature at which the total width of the structure of the lowest field lines has increased by 10%. Since Cu has a nuclear spin of 3/2 a spectrum of Cu$^{2+}$ has four hyperfine peaks. When the magnetic field is along the $c$ axis, the $g$ values are $g_{11}=2.3643$ and $g_3=2.0065$. The lowest and highest field hyperfine peaks ($I=-3/2,3/2$) are split because the Cu$^{59}$ and Cu$^{63}$ have the same nuclear spin but the magnetic moment of Cu$^{59}$ is slightly larger than that of Cu$^{63}$. The spectrum in Fig. 1 recorded at 147 K shows no splitting from magnetically non-
The phase transition temperature in Fig. 2 increases approximately linearly as the concentration decreases. One possible explanation is the freezing out of soft vibrational modes.\(^6\)\(^7\) In the theory of soft modes, the square of the frequency of the optic mode which freezes out is

\[
\omega^2 = K(T - T_c),
\]

where \(K\) is a constant, and \(T_c\) is the temperature of the phase transition.\(^6\) Our observations are in qualitative agreement with this theory. The vibrational modes of the lattice are changed by the substitution of copper for cadmium. This should be thought of as a small perturbation in the mode frequencies since the amount of copper in the crystal is very small. Copper is lighter than cadmium and therefore the frequencies of the modes increase as the amount of copper is increased. At a temperature \(T\) near the phase transition temperature a larger frequency in Eq. (1) requires a larger temperature difference between \(T\) and \(T_c\), and thus a lower \(T_c\) for a higher concentration of the copper probe. As the temperature is decreased, soft modes of vibration freeze out and the metallic ions shift to a zig-zag equilibrium position along the \(c\) axis.\(^3\)

Changes in the EPR spectra were observed for different orientations of the magnetic field with respect to the \(c\) and \(a'\) axes as a function of temperature for a number of different concentrations. When the field is oriented at 40° with respect to the \(c\) axis and 50° from the \(a'\) axis, the lowest field hyperfine lines split at the onset of the transition into doublets and there was no further change in the number of the hyperfine lines as the temperature was lowered to 20 K; however the doublet splitting increased as the temperature was lowered. At an angle of 25° to the \(a'\) axis, the lowest field lines split into triplets and at 36° they split into quartets. In all three cases, shown in Fig. 3, the splitting of the spectra began abruptly and the number of components remained the same while the width of the splitting increased as the temperature was decreased to 20 K. The smooth increase in the width of the splitting of the lowest field lines, or the order parameter, after an abrupt beginning, is characteristic of a single sec-
ond-order transition. Further support for a second-order process was the good fit of the data to the classical order parameter equation,

\[ \Delta H = \Delta H_0 (T_c - T)^\beta \]  

Here \( T_c \) is the transition temperature and \( \Delta H \) is the change in width of the lowest field peaks at temperature \( T \). Changes in the width of the lowest field lines, as the temperature decreases below the transition temperature, result from a change in the angle between the \( g_{11} \) axis of the Cu ions and the \( c \) axis of the crystal. The change in this angle is about 5° at 30 K. A graph showing \( \Delta H \) as a function of temperature is given in Fig. 4 for a sample containing 0.18% copper. The best least mean-square fit of the data to Eq. (2) for a transition temperature of 142 K gives a value of 0.30 for the critical exponent. The theoretical value for the critical exponent for a phase transition according to the Landau free energy theory should be 0.5. Our value of 0.30 is close to values often observed near 0.33 for other systems. This critical exponent may be dependent on the Cu\(^{2+}\) concentration.

In summary, our data show that the phase transition temperature in cadmium calcium acetate hexahydrate when determined by EPR of Cu\(^{2+}\) probes depends on the concentration of the Cu\(^{2+}\) probe. The observed phase transition temperature decreased from 144 to 123 K as the concentration of the probe increased from 0.07% to 1.32%. For calcium cadmium acetate hexahydrate, the EPR data are characteristic of a single second-order structural phase change with a critical exponent of 0.30. An extrapolation of the phase transition data to zero Cu\(^{2+}\) probe concentration indicates that the phase transition temperature in pure calcium cadmium acetate hexahydrate should be about 145 K.