EPR determination of three-dimensional correlations below the ferroelectric phase transition in pseudo-one-dimensional CsH_2PO_4:Cu^{2+}

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The polarization fluctuations of ferroelectric CsH_2PO_4 above T_c are generally classified as a quasi-one-dimensional phenomenon. The temperature dependence of the EPR line splitting of the $S=1$ state of the Cu^{2+} tetramer, however, exhibits a critical exponent below T_c of $\beta=0.5$ indicating that the correlations associated with the order parameter are three dimensional below T_c.

The phase transition in monoclinic CsH_2PO_4 (CDP) exhibits a number of unusual properties which are characteristic of one-dimensional systems.[1-4] The ferroelectricity in CDP is associated with the ordering of hydrogen between two equilibrium sites in the short O–H $\cdots$ O bonds linking the PO_4 groups into zigzag chains parallel to the b axis. These chains are linked into two-dimensional (2D) layers by ordered hydrogen bonds lying roughly along the c axis and cesium atoms lying between these hydrogen-bonded planes.[5] There are no hydrogen bonds along the a axis and the crystal has a cleavage plane perpendicular to the a axis. Neutron scattering studies[6] show that significant short-range order develops along the chains at a temperature well above T_c. The weaker interchain coupling responsible for the ferroelectric transition causes virtually no correlation between the layers until one gets quite close to T_c. The dielectric constant in CDP shows a crossover[4] between a region 3 K $< T - T_c \leq 90$ K dominated by 1D correlations and a region 0 K $< T - T_c \leq 3$ K dominated by 3D correlations. The 1D correlation has been confirmed by ^{31}P and deuteron resonance studies for partially deuterated CDP.[4] An apparent deviation from the quasi-one-dimensional model has been found, however, in the region of 0 K $< T - T_c \leq 20$ K by Deguchi, Okau, and Nakamura.[7] The aim of this work is to examine the temperature dependence of the order parameter of the phase transition by means of an EPR study of the line splitting for the fine-structure component of the Cu^{2+} tetramer spectrum in CDP.

CsH_2PO_4 doped with 0.3 mol% $CuCl_2 \cdot 2H_2O$ shows the usual Cu^{2+} $S=\frac{1}{2}$ single-ion spectrum at room temperature. Below about 250 K the fine-structure spectra were observed and described by us[8] as arising from the Cu^{2+} tetramers with an effective spin $S=2$ and spin-Hamiltonian parameters: $g_{\parallel}=2.2575$, $g_{\perp}=2.1866$, $D=0.181$ cm^{-1}, $E=-0.081$ cm^{-1}, $a=0.001$ cm^{-1}, $b=0$, and $c=-0.021$ cm^{-1}. Also the $0 \rightarrow -1$ transition within the $S=1$ multiplet of the tetramer was reported to have approximate[8] parameters $D_x=0.543$ and $E_x=-0.159$ cm^{-1} obtained from a phenomenological theory of the tetrameric clusters. The superexchange interaction between pairs of $Cu^{2+}(S=1)$ complexes arises through Cu-O-P-O-Cu paths. Both pairs are coupled by the hydrogen bonds along the c axis. The tetramer model is shown in Fig. 1. The excess charge compensation for the Cu^{2+} ion which replaces the Cs^+ ion is presumably provided by a proton vacancy. Figure 2 shows the EPR line splitting for the $0 \rightarrow -1$ transition for the $S=1$ multiplet versus temperature.

The EPR line position above T_c for the $0 \rightarrow -1$ transition is given by the expression[8]

$$H_0=(1/g\mu_\beta)\{h\nu+(\tfrac{1}{2})[D_x(3\cos^2\theta-1)+3E_x\sin^2\theta\cos(2\phi)]\}\ , \quad (1)$$

where θ and ϕ are the polar and azimuthal angles of the external magnetic field H_0 with respect to the x,y,z crystal-field axes. The values of D_x and E_x for $T \geq T_c$ obtained by fitting the EPR line anisotropy for the triplet spectrum are 0.462 and -0.105 cm^{-1}, respectively. The parameters D_x, E_x, and θ are not strongly temperature dependent below T_c, and the ϕ dependence below T_c is negligible since $\Delta\phi$ is less than 2°. Therefore, the equation for the line splitting below T_c can be approximated from (1) to give

$$g\mu_\beta\Delta H=3\Delta E\sin^2\theta\cos(2\phi)\ , \quad (2)$$

where ΔE arises because of the phase transition. For the external magnetic field orientation $\theta=\phi=20°$, ΔH is

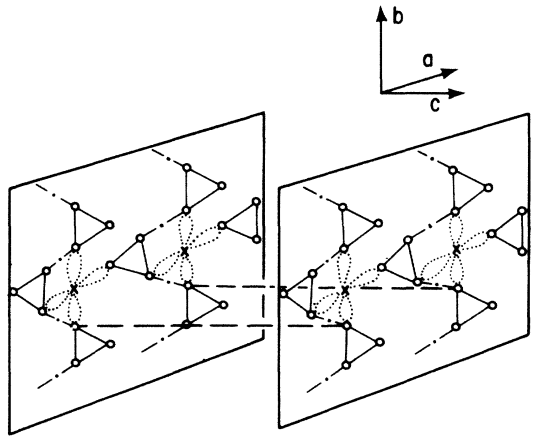

FIG. 1. Model of the tetrameric copper complex in CDP showing the superexchange paths. Two a-b planes are shown, joined along the c axis by ordered H bonds represented by a dashed line (---). Some of the disordered H bonds are represented by a dashed-dotted line (-·-·).

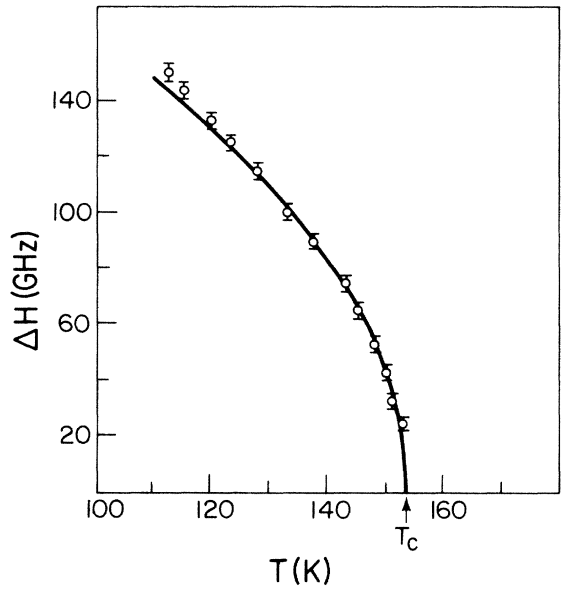

FIG. 2. EPR line splitting for $0 \rightarrow -1$ transition for $S=1$ multiplet vs temperature. Circles represent experimental data and the solid line is the fit of Eq. 4 with $\beta=0.5$.

given by

$$\Delta H(\mathrm{GHz}) = 2.64\times 10^{3}\Delta E(\mathrm{cm}^{-1}) , \quad (3)$$

with

$$\Delta E = E_x[(T_c - T)/T_c]^{\beta} . \quad (4)$$

According to Itoh, Hagiwara, and Nakamura,[9] just below T_c the ordering of hydrogen H(2) to either of the two possible sites results in a slight change of PO_4 tetrahedron orientation consisting of rotation around the P—O(2) bond and a shift of the P atom position along the b axis. These displacements are responsible for the polarization. The spin-Hamiltonian parameter ΔE should reflect these displacements and describe the temperature evolution of the phase transition order parameter.

In the temperature region $0\ \mathrm{K} < T_c - T \leq 30\ \mathrm{K}$, the ΔH_0 value is satisfactorily described by Eqs. (3) and (4) with $\beta = 0.48 \pm 0.02$ as shown in Fig. 2. This agrees within experimental error with the mean-field value of 0.5 for the critical exponent β, as expected for 3D correlations of the displacements leading to spontaneous polarization. This critical behavior of the EPR line splitting below T_c shows that the PO_4 distortion is governed by 3D correlations. Such 3D ordering of the PO_4 tetrahedra had been suggested previously by Topič *et al.*[10] from their deuteron NMR studies in CsD_2PO_4.

Results from other authors for β determined from other types of measurements are not in complete agreement. Our analysis of the spontaneous polarization (P_s) data of Yasuda *et al.*[11] for CsH_2PO_4 at 1 bar pressure yields $\beta = 0.50 \pm 0.04$ for the points within 5 K of T_c. Levstik *et al.*[12] found a linear relation between P_s^2 and T for CsD_2PO_4, indicating an exponent $\beta = 0.5$. However, Blinc *et al.*[4] found an exponent $\beta = 0.35 \pm 0.05$ for the deuterated crystal, CsD_2PO_4, from both ^{31}P NMR chemical shift and deuteron NMR measurements, and stated that this agreed with spontaneous polarization results for both CsH_2PO_4 and CsD_2PO_4 without giving a reference for the spontaneous polarization measurements.

In conclusion, our EPR results indicate 3D correlations of atomic displacements in CDP below T_c, in contrast to the 1D correlations observed above (except very near to) T_c. Discrepancies exist in the critical exponent β reported for different experiments performed below T_c. However, a β less than 0.5 could be attributed to nearness to a tricritical point (for which the mean-field β is 0.25) rather than to lower-dimensional effects.

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