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EPR STUDY OF THE SYMMETRY BREAKING EFFECT IN FERROELECTRIC CESIUM DIHYDROGEN PHOSPHATE DOPED WITH Cr^{5+} IONS

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The $(PO_4)^{3-}$ units in a CsH_2PO_4 (CDP) crystal were replaced in a small fraction of sites by $(CrO_4)^{3-}$ groups and the EPR of the Cr^{5+} center was investigated. Splitting of the EPR line appears at T_c^*=245 K, 91 K higher than the ferroelectric transition temperature T_c=154 K. The electronic wave function of $Cr^{5+}(3d^1)$ is identified as $d_{x^2-y^2}$. The $d_{x^2-y^2}$ function couples with the near protons and the reorientation of this unit in the two possible configurations occurs in the paraelectric phase and breaks the symmetry far above T_c. The observed correlation time 10^{-9} sec and associated activation energy ΔU=0.215 eV are discussed.

Introduction

Cesium dihydrogen phosphate, CsH_2PO_4 (CDP), is well known as a typical example of a hydrogen-bonded ferroelectric compound. Diffuse neutron scattering reveals the existence of one-dimensional ordering of the hydrogen bonds parallel to the ferroelectric b axis.[1] The crystal structure of CDP at room temperature has been determined by Uesu and Kobayashi,[2] and by Matsunaga, Itoh and Nakamura.[3] They showed that the symmetry is monoclinic with space group $P2_1/m$ and two formula units per unit cell. In the ferroelectric phase the space group changes to $P2_1$.

There are two kinds of one-dimensional chains of $(PO_4)^{3+}$ ions connected by hydrogen bonding.[2] One chain runs along the b axis and the other along the c axis. The phosphate tetrahedron PO_4 is deformed from a regular tetrahedron with the following distances between phosphorus and oxygen atoms:

$$P-O_1=1.607\ A^o,\ P-O_2=1.464\ A^o,$$
$$P-O_3=1.539\ A^o \text{ and } P-O_4=1.539\ A^o.$$

The length of the O-H(1)...O bonds along the c axis is 2.562 A° and they are already ordered at room temperature whereas the O-H(2)...O bond length along the ferroelectric b axis is 2.427 A° and these protons are disordered.

This result reflects the fact that a dielectric anomaly in CDP is only observed along the b axis.[4] Iwata, Koyano and Shibuya[5] report a structure determination of the low temperature phase of CDP by neutron diffraction with discussion of the transition mechanism derived from the resultant atomic shifts. They found besides the hydrogen ordering several deviations of other atoms from their symmetric positions in the paraelectric phase. The displacement of the O(1) oxygen is found to be a consequence of a small rotation of the PO_4 tetrahedron around the $P-O_2$ bond. The angle of rotation was estimated to be about 3°. Next is a displacement of the P atom along the b direction by 0.06 A°. These displacements might be responsible for generation of polarization, but the value of polarization evaluated from this model did not give good agreement with the experimental value.

In this paper we present our EPR investigation of Cr^{5+} as a dopant in a CDP crystal. There are two reasons why the Cr^{5+} probe was chosen. First, the "formal" ionic charge of the Cr^{5+} ion is the same as that of the replaced unit P, and it is near the anion site where moving of protons is expected. Second, the Cr^{5+} probe introduced by Dalal and coworkers[6,7] and Müller and Berlinger[8] into KDP family crystals has provided controversy regarding what kind of phenomena Cr^{5+} EPR spectra reflect, i.e., local dynamics of ferroelectric clusters in the paraelectric phase or Halperin-Varma-type centers.[9]

Because of the simpler proton ordering in a two-dimensional hydrogen-bond network we expected to clarify this problem in CDP:Cr^{5+} crystals.

Experimental Procedure

Single crystals of CDP were grown by evaporation from saturated water solution prepared by mixing Cs_2CO_3 and H_3PO_4 with the molar ratio 1:2 together with 0.06 mol % of K_2CrO_4.

The crystals were irradiated with a 40kV/10mA molybdenum source for 4 hours at room temperature. The EPR spectra were obtained using a Varian X-band spectrometer with 100 kHz modulation and a gas nitrogen system for temperature control and stabilization.

The orthogonal axes for the EPR measure-

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ments was chosen as a, b and c^*, with c^* perpendicular to the ab plane of the crystallographic axis system chosen by Uesu and Kobayashi.[2]

Experimental Results

At room temperature, after measuring anisotropy in the three perpendicular planes, we found that the principal axis $g_{||}$ lies in the ab plane and makes an angle of 45° with the b axis. Only one type of Cr^{5+} is observed at room temperature.

The spin-Hamiltonian used in describing the EPR spectrum has the form

$$H = \mu_B \underline{H} \cdot \underline{\underline{g}} \cdot \underline{S}. \qquad (1)$$

Because the spectrum has axial symmetry for rotation around the $g_{||}$ principal axis of the crystal field, the g parameter is described by the expression

$$g^2(\theta) = g_{||}^2 \cos^2(\theta) + g_{\perp}^2 \sin^2(\theta). \qquad (2)$$

Here θ is the angle between $g_{||}$ and the external magnetic field. *No* change in EPR spectrum was observed in the 100 to 300 K temperature region when the crystal was rotated round the b or c^* axes. Fig. 1 shows the spectrum anisotropy in the bc^* plane at room temperature and 160 K. This figure is plotted in the r, ϕ coordinate system where ϕ is the angle between the c^* axis of our orthogonal system and the magnetic field which lies along the r-axis.

As is shown in Fig. 1 the single EPR line (at 300 K) is split (at 160 K) into two lines whose g_{zz} components lie ± 45° from the b axis in the bc^* plane. Rotation of the crystal around the [011] direction gives us the g_{xx} and g_{yy} components of the g tensor at low temperature (Table I).

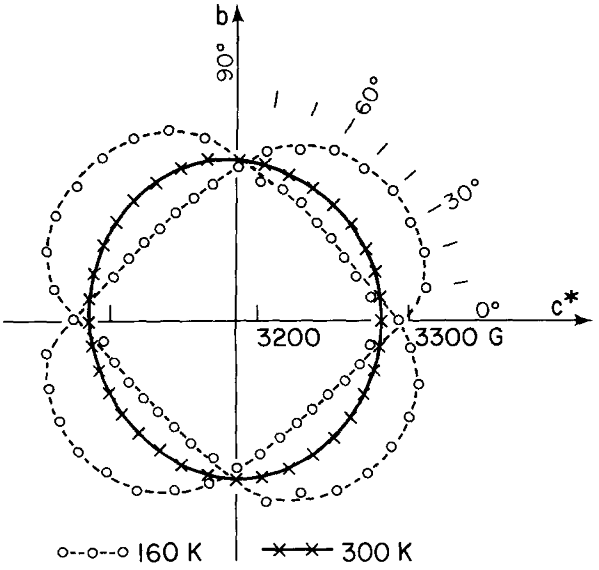

Figure 1

EPR spectrum anisotropy at room temperature (full line) and 160 K (broken line). Because of symmetry the EPR splitting can be observed only in the a rotation.

TABLE I

g at 300 K	direction cosines l m n
$g_{\|\|}$=1.9539	0.7071, 0.7071, 0
$g_{\perp}$ =1.9789	
g at 160 K	**direction cosines l m n**
g_{zz}=1.9452	0, ±0.7071, ±0.7071
g_{xx}=1.9764	0, ∓0.7071, ±0.7071
g_{yy}=1.9848	1, 0, 0

The EPR line splitting versus temperature was measured with the magnetic field parallel to the [011] direction (Fig. 2). Splitting of the EPR line appears at T_c^*=245 K, 91 K higher than the ferroelectric transition temperature.

We have used the line splitting temperature dependence to evaluate the correlation time of proton movement along the hydrogen bonds. From the Bloch equation modified by random jumps between two equally probable sites one finds[10] the complex frequencies $\omega_{\pm}$ of the doublet components as

$$\omega_{\pm} = i(\Gamma + \gamma) \pm (\delta^2 - \Gamma^2)^{1/2}, \qquad (3)$$

where 2δ is the maximum doublet splitting, Γ is the jump frequency between the two sites, and γ is the width of the individual components in the absence of jumps.

The real part of Eq. (3) gives the position of the two doublet components relative to the center of the doublet and the imaginary part

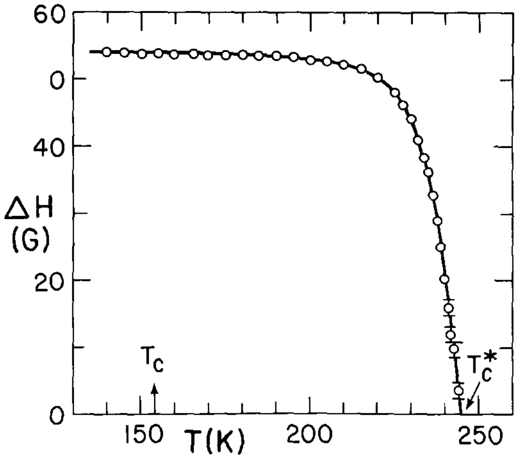

Figure 2

The EPR line splitting ΔH *vs*. temperature T for external field H_o directed along [110].

gives their width. When $\Gamma < \delta$ the singlet line change into a doublet.

The jump frequency obtained from Eq. (3) is

$$\Gamma = 0.5[(2\delta)^2 - (\Delta\omega)^2]^{1/2}, \tag{4}$$

or

$$\Gamma = (g\mu_B/2\hbar)[(\Delta H_o)^2 - (\Delta H_t)^2]^{1/2}, \tag{5}$$

where ΔH_o is the maximum doublet splitting value in gauss and ΔH_t the splitting at given temperature.

Taking into consideration the g=1.967 value of the center of the doublet we have the following expression for the jump frequency in our experiment:

$$\Gamma = 8.65\text{x}10^6[\Delta H_o)^2 - (\Delta H_t)^2]^{1/2}. \tag{6}$$

The plot of $\ln\Gamma$ vs. $10^3/T$ shown in Fig. 3 can be described by the simple Arrhenius law

$$1/\tau_c = (1/\tau_{co})\exp(U/kT), \tag{7}$$

where $1/\tau_c = \Gamma$, $1/\tau_{co} = 1.38\text{x}10^{13}$ sec and $\Delta U = 0.215$ eV except in the narrow region about 5 K below T_c^*. The critical slowing down effect in CDP was measured by Kanda *et al.*[11] in the frequency region below 1 GHz. The independent-dipole relaxation time, which is governed by the hopping of protons between the double well potential minima in the high temperature region, was $\tau_o = 1.9\ 10^{-13}$ sec. They get the τ value of the ferroelectric relaxation mode by the following expression which is valid for a pseudo-one dimensional Ising system above T_c:

$$\tau = \frac{\tau_o \cosh(2\beta J_{||})T_c}{\beta_c J_{|}(1 - 2\beta_c J_{||})(T - T_c)} \tag{8}$$

For CDP the observed temperature dependence of the relaxation time was fitted with the following parameters: $J_{||}/k = 234$ K is the intrachain interaction constant, $J_{\perp}/k = 6.78$ K is the interchain interaction constant, $\beta = 1/kT$, and $\beta_c = 1/kT_c$. By using Eq. (9) we obtain in the 200 to 245 K temperature region the range of values $\tau_c^{-1} = (0.58-1.70)\text{x}10^{11}$ sec^{-1} to compare with our experimental value range $\tau_c^{-1} = (3.3-4.6)\text{x}10^8$ sec^{-1}.

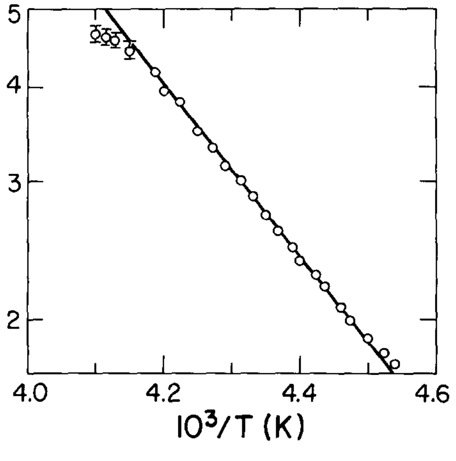

Figure 3
The $\ln\Gamma$ *vs.* $10^3/T$ plot.

The change of the g_{zz} directions by ± 45° from the *b* axis requires a corresponding reorientation of the CrO_4 tetrahedron or reorientation of the $d_{x^2-y^2}$ orbital of the Cr^{5+} ion. Such $d_{x^2-y^2}$ orbital pivoting seems more reasonable and has been well established by ENDOR and EPR data for Cr^{5+} in KH_2AsO_4.[8,12]

Fig. 4 shows the hypothetical pivoting of the $d_{x^2-y^2}$ orbital due to interaction of the negatively charged orbital with the positive protons.

The relation $g_{||} < g_{\perp}$ between the experimental values of the g-tensor components leads to the conclusion that the $d_{x^2-y^2}$ orbital of the Cr^{5+} ion has lowest energy[8] and is perpendicular to the $g_{||}$ direction above T_c^*. Above T_c^* the $g_{||}$ axis lies along the [110] direction but below T_c^* it lies along the [011] and $[0\bar{1}1]$ directions. Such changing of the principal axes requires pivoting of the y^2 lobe around the *c** axis due to the interaction with the protons in *c*-axis bonds which are ordered above T_c.

Due to coupling of the $d_{x^2-y^2}$ orbital to the nearest two protons we observe in the EPR spectrum a symmetry breaking effect when the frequency of reorientation of the Cr^{5+} centers associated with *b*-bond proton jumping is lower than our EPR frequency.

Discussion

Much interest has recently centered on the possible existence of a dynamic central peak (CP) near structural and ferroelectric phase transitions. There are two points of view on the physical origin of CP phenomena. First, some have ascribed the CP dynamics to a pure lattice excitation,[13,14] that is, an intrinsic phenomenon. In accord with this view, when the transition is approached from above T_c, regions

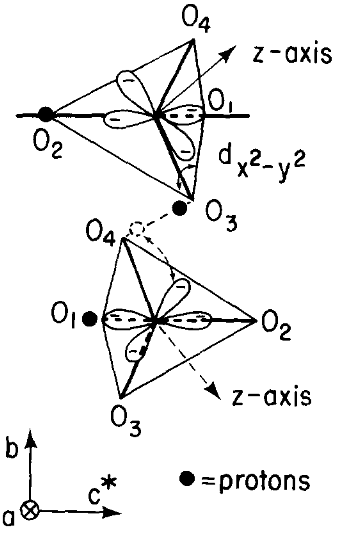

Figure 4
Schematic reorientations of $d_{x^2-y^2}$ orbital due to moving in hydrogen bonds.

with the short range order and symmetry of the low temperature phase start to appear. The other possibility is that the CP mode is due to presence of impurities or other defects.[15]

Halperin and Varma[9] considered a model in which the distortion in a defect unit cell may jump between orientations which break symmetry, a situation they describe as a relaxing defect cell. The first EPR identification of this kind of center was made by Müller *et al.*[8] for Cr^{5+} in a KH_2AsO_4 crystal.

Within the relaxing Halperin-Varma model the reorientational correlation time τ of the defect is related to the central peak width Γ by the relation

$$\Gamma = \omega_s^2/\tau(\omega_s^2+b^2) \qquad (9)$$

where $\omega_s^2=A(T-T_c)$ is the soft mode frequency and b^2 is proportional to the defect concentration. A defect concentration of order 10^{-5} is sufficient for explaining the CP width in this model.[9] In our experiment the fractional Cr^{5+} concentration was about 10^{-3}. However, Γ cannot be fitted by Eq. (10) but rather by a simple activation process for which $\Gamma = 1/\tau$.

On the other hand the presence of ferroelectric clusters far above T_c with a size of order 10^2 A^o in CDP has been well established by a neutron scattering experiment.[1]

It is our opinion that the ferroelectric clusters far above T_c are "pinned" and stabilized by the defect center and by the height of the barrier for the *b*-bond protons which are coupled with the $d_{x^2-y^2}$ orbital.

As a result the jump frequency for the protons interacting with the defect is about 10^3 times lower than in undisturbed parts of the crystal. The defect center and associated pinned cluster are switched by the arrival of clusters of an opposite polarity and not by the soft mode fluctuation.

A similar explanation has been made by Gonzaga *et al.*[10] for behavior of $(AsO_4)^{4-}$ centers in ADA-ADP mixed crystals.

The values obtained for τ and ΔU for CDP:Cr^{5+} as well as the flattening of the ln $1/\tau$ versus $10^3/T$ plot near T_c^* are quite similar to the results obtained by Lamotte *et al.*[16] for $(AsO_4)^{4-}$ radicals in KDA. The flat portion of the ln Γ curve in our case with the activation energy $\Delta U=0.05$ eV and typical $\tau_o=10^{-12}$ sec value gives $\tau=10^{-11}$ sec and can be connected with off-center motion of Cr^{5+} ions along the *b* axis which can explain the nonaxial g tensor below T_c^*.

It follows that the cooperative dynamics around Cr^{5+} cannot be intrinsic.

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