EPR STUDY OF MONOCLINIC RbD$_2$PO$_4$ MONOCRYSTAL DOPED WITH Cr^{5+} ION

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Deuterated monoclinic RbD$_2$PO$_4$ (DRDP) doped with chromium Cr^{5+} is studied by EPR in 90 K to 400 K temperature range. EPR reveals two types of paramagnetic centers: single Cr^{5+} ($S = 1/2$) complex and Cr^{5+}–Cr^{5+} coupled pairs with effective spin $S = 1$. The EPR line splitting of single Cr^{5+} complex in DRDP versus temperature agrees with the unit cell multiplication. The splitting of EPR line of pair spectrum appears at $T^* = 160$ K, far below the phase transition temperatures and is due to the anisotropy of the exchange interaction. The clustering effect in the low-dimensional DRDP is suggested.

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1. Introduction

Deuterated rubidium dihydrogen phosphate RbD$_2$PO$_4$ (DRDP) crystallizes stably to monoclinic system at room temperature [1] and undergoes successive phase transitions [2] at 377 K (T_I) and 317 K (T_{II}). The sequence [3] of phase transitions with decreasing temperature is

$$P2_1/m(a_0, b_0, c_0) \Rightarrow P2_1/c(a_0, b_0, 2c_0) \Rightarrow P2_1(2a_0, b_0, 2c_0).$$

The crystal at the room temperature phase below T_{II} is ferrielectric and is not polar in the intermediate phase below T_I. Ferrielectric activity [4, 5] observed along b-axis can be understood in terms of a sublattice formation.

There are two kinds of hydrogen (deuterium) bond chains: one along b-axis and the other along c-axis. The deuterium atoms in the former chains are ordered

in phase III and disordered in phases I and II, while those along c-axis are ordered even in phase I [5].

Recently complex dielectric measurements [6] in the frequency range 10^6–10^8 Hz as well as NMR studies of ^{87}Rb [17] revealed the pseudo one-dimensional nature of the correlations in the deuterium motion between the two potential minima in the O–D...O bonded chains along b-axis. This motion freezes out at T_{II}.

In order to throw some light on the microscopic nature of the phase transition in DRDP we introduce the Cr^{5+} paramagnetic probe and study its EPR spectrum as a function of temperature.

There were three reasons why the Cr^{5+} probe was chosen. Firstly, the "formal" ionic charge of Cr^{5+} ion is the same as that of replaced unit P and it is placed at the anion site surrounded by deuterons. Secondly, the Cr^{5+} probe was successfully used to study the so-called "symmetry breaking effect" in KDP crystals family [7–13]. Thirdly, the pseudo one-dimensional ordering (1D) of deuterons should somehow be reflected in EPR spectra.

2. Experimental

Deuterated single crystal of monoclinic DRDP were grown following the procedure described elsewhere [6] and in addition 0.06 wt% of $K_2Cr_2O_7$ was added to the mother solution.

Chromate $(CrO_4)^{2-}$ anions replace small amount of PO_4^{3-} tetrahedra in RbD_2PO_4 single crystal. In order to generate $(CrO_4)^{3-}$ paramagnetic probe (spin $S = 1/2$) the crystal was X-irradiated with 40 kV/10 mA wolfram source for 4 h at room temperature.

The dielectric permittivity ε_b was also measured by us and confirmed ε_b anomaly at 317 K as reported for deuterated DRDP [14]. EPR spectra of Cr^{5+} paramagnetic ion were measured with X-band spectrometer operating with liquid nitrogen system of temperature control and stabilization.

The orthogonal XYZ axes for EPR anisotropy measurements were chosen as $Z \parallel c$, $Y \parallel b$ and $X \parallel (a \times b)$ of the crystallographical a, b, c axes [5].

3. Experimental results

The EPR spectra of Cr^{5+} $(S = 1/2)$ ion consist of four narrow lines and one broad single line hardly visible at room temperature. The EPR spectra at 93 K and 290 K temperatures are shown in Fig. 1. The weak lines marked by arrows are the deuterium trapped hyperfine structure.

From measuring the EPR line anisotropy in three perpendicular planes at room temperature, we find that $g_\parallel$ of principal axis of Cr^{5+} complex is directed along $(b \times c)$ axis and $g_\rceil$ coincides with b-axis.

The spin Hamiltonian used to describe the EPR spectrum is

$$H = gBBS \tag{1}$$

and EPR spectrum of $Cr^{5+}(S = 1/2)$ ion with axial symmetry exhibits the anisotropy described with the $g(\Theta)$ function

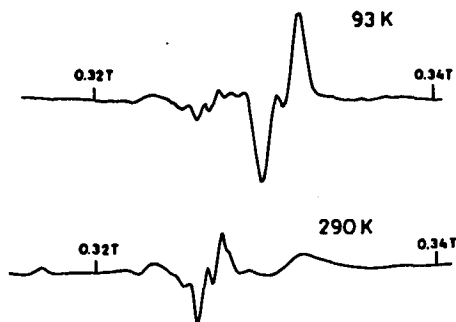$$g^2(\Theta) = g_\parallel^2 \cos^2(\Theta) + g_\rceil^2 \sin^2(\Theta). \tag{2}$$

Fig. 1. The EPR spectra of Cr^{5+} in RbD$_2$PO$_4$ at 290 K and 93 K: narrow lines — single Cr^{5+} ($S = 1/2$); broad line — Cr^{5+}–Cr^{5+} pairs spectra; weak lines marked by arrows — deuterium trapped spectrum.

Here Θ is the angle between $g_{\parallel}$ and the external magnetic field B, B is Bohr magneton, and $g_{\parallel} = 1.947$ and $g_{|} = 1.973$ at 377 K. The relation $g_{\parallel} < g_{|}$ allows to conclude that the lowest orbital of single Cr^{5+} complex is $d_{x^2-y^2}$. At room temperature when the external magnetic field B is along b at $g_{\parallel} = 1.9500$ a broad line is observed and four patterns of narrow lines are centered at $g_{|} = 1.9795$ value. Figure 2 shows the line position in magnetic field versus temperature for broad (full circles) and narrow lines (open circles and crosses) for this orientation.

The four narrow Cr^{5+} EPR lines recorded at room temperature are due to doubling of the unit cell of DRDP along c-axis below T_{I} (377 K) and next doubling along a-axis below T_{II} (317 K). Thus, the EPR confirms the unit cell multiplication in accordance with NMR and X-ray studies [17, 5].

Another effect is observed for the broad EPR line which undergoes the line splitting into two components of equal intensity at 160 K (Fig. 2) which may be not related to phase transitions. Figure 3 shows the intensity of the broad line (crosses) and its linewidth ΔB_{pp} anomalies (open circles) versus temperature. For comparison, the intensity of narrow line spectra (open triangles) decreases with the temperature lowering and does not follow Curie law C/T as could be expected. Their line widths are temperature independent.

The integral intensity of the broad signal as a function of temperature is displayed in Fig. 4, where the open circles are the experimental data and the solid line is the best fit calculated with exponential function $A = A_0 \exp(600/T)$.

The broad EPR line is due to exchange interaction between Cr^{5+} complexes ($S = 1/2$). The activation energy 600 K ($J = 518$ cm^{-1}) used for integral intensity line fit (Fig. 3) would then correspond to the singlet–triplet separation between $0\rangle$ and $\mp 1\rangle$ spin states.

Below $T^* = 160$ K the line splitting arises due to anisotropic part of the spin-exchange integral [16]. This means that the spin–spin interaction energy is also dependent on orientation of the exchange coupled spins relative to their environment in the crystal [15].
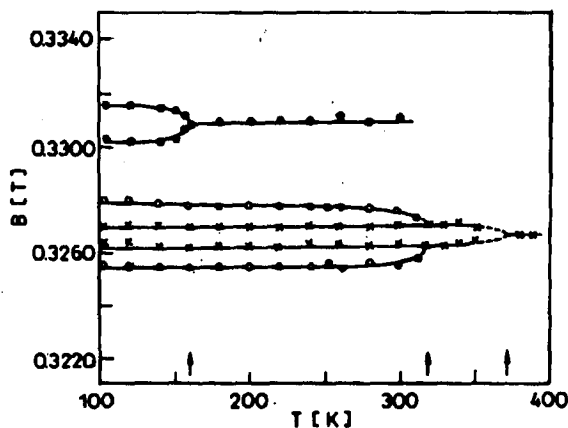
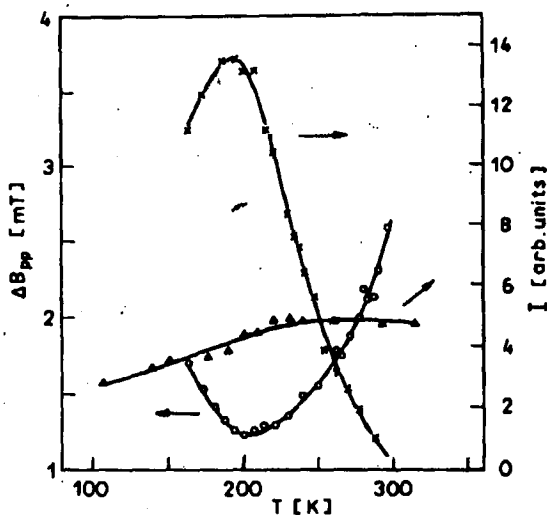Fig. 2. The EPR line positions versus temperature for single Cr^{5+} — crosses and circles, and pairs spectra — full circles.

Fig. 3. The temperature dependencies of the broad line intensity (crosses), linewidth anomaly (circles) and single Cr^{5+} line intensity (triangles).

Spin Hamiltonian describing this splitting has the form [15]:

$$H = g_z\beta B_z T_z + (1/2)(J'_x T_x^2 + J'_y T_y^2 + J'_z T_z^2), \tag{3}$$

where $T_i = S_{1i} + S_{2i}$, $i = x, y, z$ are the local crystal field axes, and the first term describes Zeeman energy, second-anisotropic exchange (with $\sum J'_i = 0$).

If $g_z\beta B_z \gg J'$, the spin allowed transitions are just those within triplet for which $\Delta m = \mp 1$, and occur for $z \parallel B_0$ at

$$h\nu = g_z\beta B_z \pm (3/4)J'_z. \tag{4}$$

Hence the magnitude of J'_z can be evaluated from the line separation below T^* and at 100 K it is equal to 1.3 mT or 1.2×10^{-3} cm^{-1} in energy units.
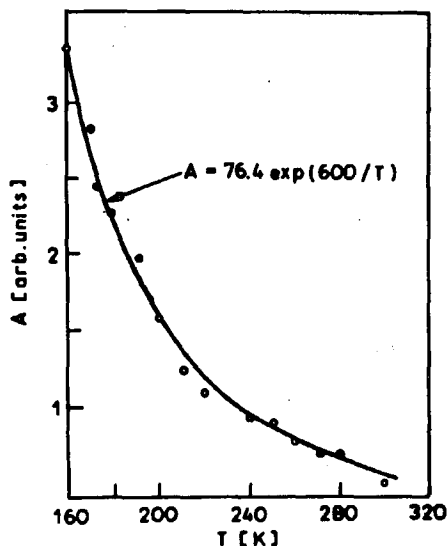
Fig. 4. The integral intensity of the broad line versus temperature: circles — experimental, solid line — fit in accordance with $A = 76.4\exp(600/T)$.

The anomaly of the broad EPR linewidth is due to the anisotropic exchange J' magnitude. J'_z value can also be estimated from the relation between the measured ΔB_{pp} linewidth and its $\langle \Delta B \rangle^2$ second moment according to the formula [16]:

$$\Delta B_{pp} = \langle \Delta B \rangle^2 / \omega_e, \tag{5}$$

where ω_e is the exchange frequency. The value of $J'_z = \hbar\omega_e$ is the same as the one previously obtained from the line separation.

4. Discussion

It is well known, from the numerous studies of anionic EPR centers in KDP-like crystals [8–14], that the effects of line splitting occur at T^* temperatures well above T_C. There is also disagreement on what actually these splittings are: precursor of ordered phase or the local defect soft mode.

In the case of DRDP:Cr^{5+} we observe the isolated Cr^{5+} ($S = 1/2$) complexes, EPR line of which splits at T_I, T_{II}, T_{III}, temperatures at which the structural phase transitions in pure DRDP were recorded [1–3, 14].

Using the defects classification of Halperin and Varma [18] we can attribute our Cr^{5+} center as "frozen defect cell" for which the contribution to the order parameter is $\langle \Phi^2 \rangle \sim (T - T_c)^{0.5}$. In addition we observe Cr^{5+}–Cr^{5+} pair EPR spectrum of the two coupled centers through O–D. . . O path, line splitting of which at T^*, well below T_{III}, is due to the anisotropic part of exchange coupling J'. It has been shown by dielectric measurements [6] that the strength of one-dimensionality in DRDP is equal to 1.43×10^4 compared with the value 1.33×10^2 of CsH₂PO₄ (CDP) crystal. It is worth noticing that the coupling of four Cu^{2+} paramagnetic

centers in CDP was also observed by us [19, 20]. This means that contrary to 3D ordered KDP-like crystals low dimensionality of DRDP and CDP prefers the exchange coupling of paramagnetic center. The full explanation of these preferences needs further studies of other hydrogen bonded low dimensional crystals. The theoretical explanation of ESR spectra based on the interchain and intrachain spin couplings is well established in low dimensional magnetic systems [21, 22] but it is not the case of our ferroelectrically ordered and magnetically diluted system. At present we cannot rule out the possibility that $Cr^{5+}-Cr^{5+}$ clusters are formed randomly in crystal during crystal growth. Further experiments are in progress.

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