Optical detection of a pseudonuclear Zeeman effect in a triplet state

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(Submitted 13 April 1979)

Pis'ma Zh. Eksp. Teor. Fiz. **29**, No. 11, 692–696 (5 June 1979)

Anomalously high splitting of the $I = 1/2$ spin state of a P^{31} nucleus is observed in the optically-detected spectrum of $KC1\text{-}PO_2^-$ magnetic resonance in weak magnetic fields up to 500 Oe. The splitting is interpreted as a pseudonuclear Zeeman effect which occurs when the nuclear and electron spins are coupled in the second order perturbation theory.

PACS numbers: 33.25.Fs, 33.20.Kf

Anomalies in the hyperfine structure of the EPR spectra of rare-earth ions were observed.[1] Interpreted as a pseudonuclear Zeeman effects, these second-order corrections involving adjacent excited electronic levels were considerably in excess of the natural nuclear Zeeman splitting which occurs in the first order.

A similar phenomenon is possible in the molecular triplet state in which the role of closely-spaced intermediate levels is played by the very splitting sublevels in the zero field, the expected effect being much more intense due to the small separation between the levels. In particular, in the presence of a single nucleus with spin $I = 1/2$ the hyperfine coupling (HFC) between the nucleus nuclear and electrons in a zero field results only in a displacement of spin sublevels while Kramer's double degeneracy is removed in an external magnetic field.

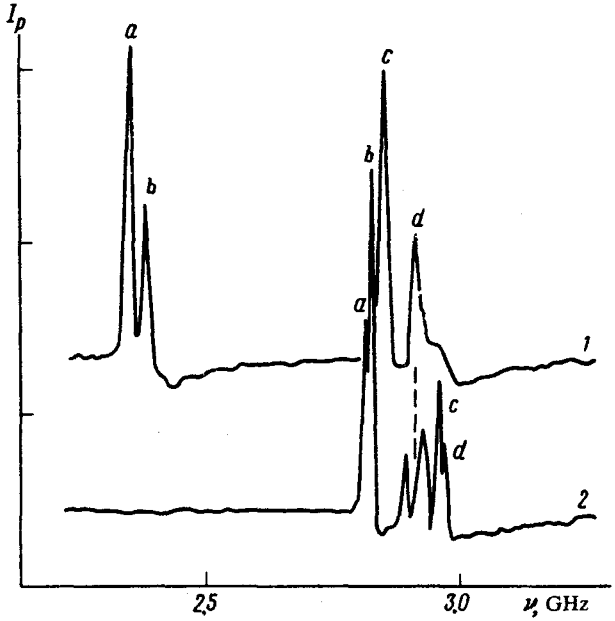

FIG. 1. ODMR spectra of KCl-PO_2^- crystal in magnetic fields $H = 500$ Oe(1) and 100 Oe(2) for orientation $H \| \langle 110 \rangle$, $T = 4.2$ K.

The foregoing situation exists in an impurity ion PO_2^- which contains a P^{31} nucleus with spin $I = 1/2$. A KCl-PO_2^- single crystal was used as a specimen,[2] whose phosphorescence spectra are characterized by a quasilinear structure typical of light impurity molecules.[3,4] Effect of a magnetic field of the spin subsystem of an impurity center was studied by the method of optical detection of magnetic resonance (ODMR), which provides a high sensitivity measurement (see, for example, Ref. 5).

The ODMR spectra were measured by means of an established procedure[6] in a rapid transmission mode. The microwave field source consisted of oscillating frequency generators P2-11 (1.5–3 GHz) and XI-30 (0.2–1.5 GHz), which were synchronized with the signal build-up cycle in the LP-4840 analyzer. An optical portion of the helium cryostat was placed between the poles of a Takeda Riken 308 electromagnet.

In a zero field, KCL-PO_2^- exhibits strong ODMR resonance at 2.93 GHz,[7] corresponding to a transition between the T_y and T_z sublevels of the triplet state ${}^3B_1$ (the y and z axes lie in the plane of molecule). We showed that this line splits into a number of components (Fig. 1), even in very weak magnetic fields beginning with $H \approx 20$ Oe. Some splitting occurs as a result of nonequivalence of the various orientations of the impurity ion with respect to the field. For $H \| \langle 110 \rangle$, three nonequivalent types of centers exist, for one of which $H \| z$. In this type of center, the $T_y - T_z$ transition frequency decreased to 400 MHz with field growth and was followed by "anti-intersection" of levels (also identified for organic molecules[8]). We interpret the four-component structure, consisting of lines a,b and c,d (Figs. 1 and 2) as hyperfine splitting which has, in the weak fields, the nature of a pseudonuclear Zeeman effect.

The spin Hamiltonian for a triplet state in the presence of a single nucleus with $I = 1/2$ may be expressed as follows:

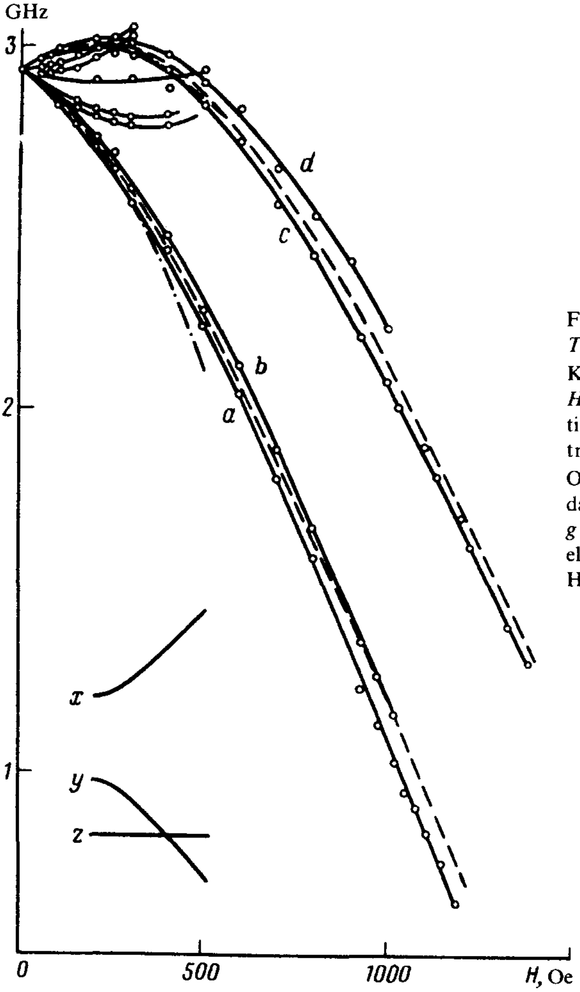

FIG. 2. Dependence of line splitting of $T_y - T_z$ transition in ODMR spectrum of KCl-PO_2 on magnetic field intensity, $H \| \langle 110 \rangle$. Dotted lines indicate approximation by means of diagonalizing Eq. (2) matrix for $A_{xx} = 100$, $A_{zz} = 400$, $A_{yy} = 250$ Oe (small splitting of Z^{+} disregarded); dash-dot lines–approximation by Eq. (3); $g = 2$ and $X - Y = 4.6$ GHz.[7] Below, level diagram for $H \| z$ without allowance for HFC.

$$\mathcal{H}_s = -(XS_x^2 + YS_y^2 + ZS_z^2) + g\beta \mathbf{HS} + \mathbf{S}A\mathbf{I} + g_N\beta_N\mathbf{HI}, \qquad (1)$$

where X,Y,Z are zero-field energies without allowance for HFC and β and β_N are the electron and nuclear magnetons; the g-tensor is considered to be isotropic. As base functions we shall pick the following zero-field states; electron $|x\rangle, |y\rangle, |z\rangle$ and nuclear $|\pm 1/2\rangle$; moreover, in the case $H \| z$, the latter may also be quantized in the z direction. Thus, a 6×6 matrix of $\mathcal{H}_s$ elements is decomposed into two 3×3 matrices

$$|x, \pm \frac{1}{2}> \qquad |y, \pm \frac{1}{2}> \qquad |z, \mp \frac{1}{2}>$$

$$\begin{bmatrix} X \pm \frac{1}{2} g_N \beta_N H_z & i(g\beta H_z \pm \frac{1}{2} A_{zz}) & \mp \frac{1}{2} A_{yy} \\ -i\left(g\beta H_z \pm \frac{1}{2} A_{zz}\right) & Y \pm \frac{1}{2} g_N \beta_N H_z & \frac{i}{2} A_{xx} \\ \mp \frac{1}{2} A_{yy} & -\frac{i}{2} A_{xx} & Z \mp \frac{1}{2} g_N \beta_N H_z \end{bmatrix} . \tag{2}$$

Allowing for second-order corrections, we get

$$Y^{\pm} = Y \pm \frac{1}{2} g_N \beta_N H_z + \frac{\left(g\beta H_z \pm \frac{1}{2} A_{zz}\right)^2}{Y - X} + \frac{A_{xx}^2}{4(Y - Z)} , \tag{3}$$

and, likewise, for $X^{\pm}$. The splitting of the Y level in this approximation is

$$\Delta_{\pm}^{(y)} = \left(g_N \beta_N + 2 g \beta \frac{A_{zz}}{Y - X}\right) H_z . \tag{4}$$

The foregoing clearly indicate that a second-order correction for HFC is similar to the nuclear Zeeman term, i.e., it induces a pseudonuclear Zeeman splitting. As a rule, $g_N \beta_N H_z$ may be neglected in weak fields. The Z level undergoes HFC splitting in higher orders, if $A_{xx}, A_{yy} \neq 0$. For noncanonical orientations, **I** fails to quantize exactly with respect to **H** and the formulas become more complex. A similar problem was also considered in a strong–field approximation.[9]

The splitting observed in KCl-PO_2^- is very small interpreted within the framework of the treatment above. The HFC atomic parameters of the P^{31} nucleus are $A^*_{iso} = 3460$ Oe and $2B^* = 206$ Oe,[10] which indicate that substantial splitting may be expected. The spacing between the doublets *a,b* and *c,d* (Fig. 2) corresponds to splitting of the Y-level into the Y^+ and Y^- components, and the doublets themselves to the splitting of the Z-level. The experimental data points for the centers $H \| z$ are sufficiently well described by the eigenvalues $Y^{\pm}$ and $Z^{\pm}$ of the matrix in Eq. (2) for $A_{zz} = 400 \pm 20$ Oe; an exception to this is the splitting of the Z-level which exceeds the expected magnitude for reasons explained by a nonideal orientation. We should note that A_{zz} determines a value of H_z for which a displacement of the Y^- level changes sign. Study of the orientation relationships of the splitting diagram confirms the above interpretation and yields the values $A_{xx} \approx 100$ Oe and $A_{yy} \approx 250$ Oe. For $H \| z$ nondiagonal elements A_{xx} and A_{yy} play an important role in the intersection region, causing a repulsion (anti-intersection) of the Y^+, Z^- and Y^-, Z^+ levels. The measured value of repulsion $V \approx 300$ MHz fully agrees with a value predicted on the basis of Eq. (2), and requires no introduction of additional perturbations.

The observed effect of pseudonuclear Zeeman splitting offers a means of investigating HFC in weak magnetic fields which, in conjunction with ODMR, provides high sensitivity in the structural study of impurity molecules.

The authors thank K.K. Rebane for interest in this work.

[1] B. Blini, Sb. Sverkhtonkiye vzaimodeĭstviya v tverdykh telakh (Coll. Hyperfine Coupling in Solid State), E.A. Turov, Ed., M., Mir, 1970, p. 15.

[2] B.T. Plachenov, V.P. Avdonin, G.A. Mikhal'chenko and V.M. Smagin, Izv. ANSSSR, Ser. Fiz. **30**, 959 (1972).

[3] R.A. Avarmaa, Opt. Spektrosk. **32**, 959 (1972).

[4] K.K. Rebane and L.A. Rebane, Pure Appl. Chem. **37**, 161 (1974).

[5] J. Schmidt, IN: Magnetic Resonance and Related Phenomena, Proc. XIX Congress Ampere, Heidelberg, 1976, p. 105.

[6] A. Suisalu and R. Avarmaa, Izv. AN Est SSR, fiz. mat. **27**, 217 (1978).

[7] S.J. Hunter, K.W. Hipps and A.H. Francis, Chem. Phys. Lett. **51**, 287 (1977).

[8] W.S. Veeman, A.L.J. van der Poel and J.H. van der Waals, Mol. Phys. **29**, 225 (1975).

[9] J.A. Mucha and D.W. Pratt, J. Chem. Phys. **66**, 5356 (1977).

[10] P. Atkins and M. Simons, Spektry EPR: stroenic neorganicheskikh radikalov (EPR Spectra and the Structure of Inorganic Radicals), M., Mir, 1970.