

# Determination of signs of parameters of hyperfine and super-hyperfine interactions

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A simple method is proposed for determining the signs of hyperfine (HF) and super-hyperfine (SHF) interactions for  $S = 1/2$ .

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The method of determining absolute signs of parameters of HF and SHF interactions for paramagnetic impurity centers with  $S \gg 1$  by means of double electron-nuclear resonance (DENR) was developed earlier.<sup>[1]</sup> Methods of finding the signs of components of the SHF tensor on the basis of methods of triple electron-nuclear-nuclear resonance and rf discrete saturation were considered elsewhere.<sup>[2,3]</sup>

In this work we propose a simple method of determining the signs of the HF and SHF interactions using the experimental DENR data. The method is based on the fact that in the presence of HF interactions in a paramagnetic system the electron spin  $S$  in the presence of a constant external magnetic field  $H$  is not quantized along the direction of that field but in line with the effective field generated by the vector addition of  $H$  and the hyperfine field. This leads to the projection of  $S$  in the direction of the  $H$  field being different from the values  $\pm \frac{1}{2}$ . The magnitude of the reduced  $S_z$  is calculated by means of wave eigenfunctions for each HF state obtained as a result of diagonalizing the spin Hamiltonian. For example,  $S = \frac{1}{2}$  for both the electron and nuclear spins. The expected value  $\langle S_z \rangle$  is

$$\langle S_z \rangle = \frac{M[g\beta H + A(M + m)]}{[A^2 + 2g\beta H(M + m)A + (g\beta H)^2]^{1/2}},$$

where  $M$  and  $m$  are electron and nuclear quantum numbers, respectively, and  $A$  is HF interaction constant.

In the experiment,  $\langle S_z \rangle$  variations show up as frequency-shifted DENR lines when observed at different EPR lines. This precise fact is used to find the signs of parameters of the HF and SHF interactions, a task consisting of three stages.

The first stage consists of single-valued identification of lines of remote coordinating domains of ligands in the DENR spectrum with respect to electron states. This is relatively simple to accomplish due to the almost dipole nature of interaction between the paramagnetic center and remote ligands.

The second stage is based on the fact that  $\langle S_z \rangle$  clearly depends to a considerable degree on the sign relationships of  $M$  and  $m$ , i.e., on the sign of  $A$ . The frequency shift of the DENR lines (for example, the second coordination ligand domain), occasioned by a change in  $\langle S_z \rangle$ , permits a direct identification of the HF components of the EPR spectrum with respect to  $m$ , i.e., allows determination of the actual sign of  $A$ .

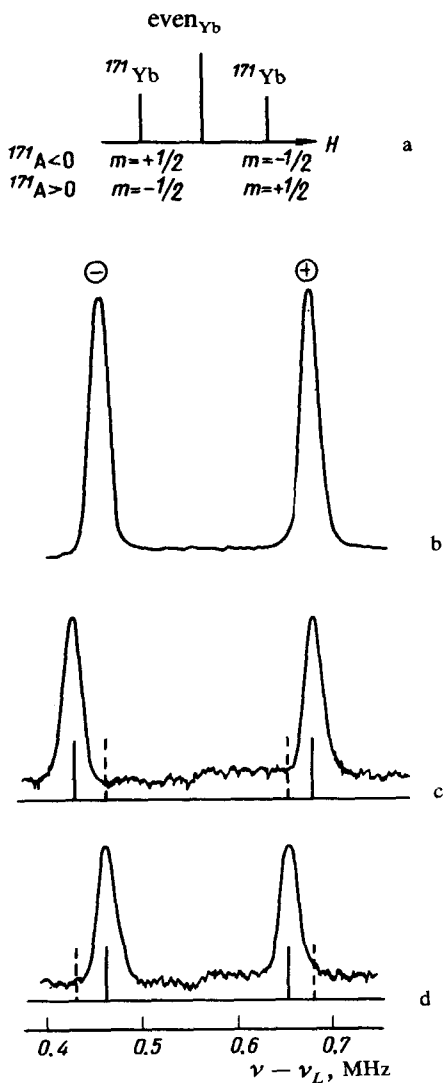


FIG. 1. EPR spectrum of  $\text{KZnF}_3 : \text{Yb}^{3+}$  and a portion of the experimental DERN spectrum—2nd coordination domain lines  $^{19}\text{F}$  observed at  $^{\text{even}}\text{Yb}^{3+}$  (b), low-field (c), and high-field (d)  $^{171}\text{Yb}^{3+}$  EPR lines. Solid vertical lines in (c) and (d)—calculated DERN lines at  $^{171}\text{A} < 0$ , dash lines—at  $^{171}\text{A} > 0$ . +, — affiliation of DERN lines to electron states  $S_z = \mp \frac{1}{2}$ , respectively;  $\nu_L$  is the Larmor frequency  $^{19}\text{F}$ .

The third stage is associated with finding signs of parameters of the SHF interactions in the first ligand coordination domain. Since the real value of  $\langle S_z \rangle$  is fixed, the DENR lines of this domain with respect to frequency shift are uniquely identifiable from the electron states which directly determines the signs of the SHF interaction parameters.

Procedures for finding signs of the HF and SHF interactions are further simplified in the presence of even and odd isotopes of the paramagnetic ion. The positions of

the DENR lines associated with an isotope constitute reference points. They may be used to directly fix the frequency shift of the corresponding DENR lines due to odd isotopes.

The proposed method was used in the study of  $^{171}\text{Yb}^{3+}$  in the crystals  $\text{KMgF}_3$  and  $\text{KZnF}_3$ . Figure 1 shows a portion the DENR spectra observed for the even and odd isotopes  $^{171}\text{Yb}^{3+}$  in  $\text{KZnF}_3$ . Clearly, a frequency shift is observed in the experiment. A comparison of the experimental and calculated spectral lines—using the expression for  $\langle S_z \rangle$ —directly establishes that  $^{171}\text{A}$  has a negative sign. Similarly, we find the line distribution of the first coordination domain with respect to electron states. In this manner, we for the first time experimentally determined the absolute signs of the isotropic ( $A_s > 0$ ) and anisotropic ( $A_p < 0$ ) parts of SHF interactions for six-fold coordination, and the absolute signs of the HF interaction parameters ( $^{171}\text{A} < 0$ ,  $^{173}\text{A} > 0$ ).

<sup>1</sup>M.L. Falin, V.P. Meiklyar, and M.M. Zaripov, *Phys. Stat. Sol. (b)* **72**, K133 (1975).

<sup>2</sup>R.J. Cook and D.H. Whiffen, *Proc. Phys. Soc.* **84**, 845 (1964).

<sup>3</sup>R.I. Mirrianshvili, O.V. Nazarova, and T.I. Sanadze, *Pis'ma Zh. Eksp. Teor. Fiz.* **23**, 556 (1976) [*JETP Lett.* **23**, 510 (1976)].