ıetermination of the sign of the components of ıe tensor of the ligand hyperfine interaction

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A method is proposed for determining the sign of the components of the ligand hyperfine interfine (HFI) tensor by radiofrequency discrete saturation (RFDS). Owing to the pulsed action of the microwave and RF fields, the relaxation processes play no role in a multilevel spin system, and the RFDS method can be successfully used in the case when the signs of the HFI parameters cannot be determined by triple electron-nuclear-nuclear resonance.

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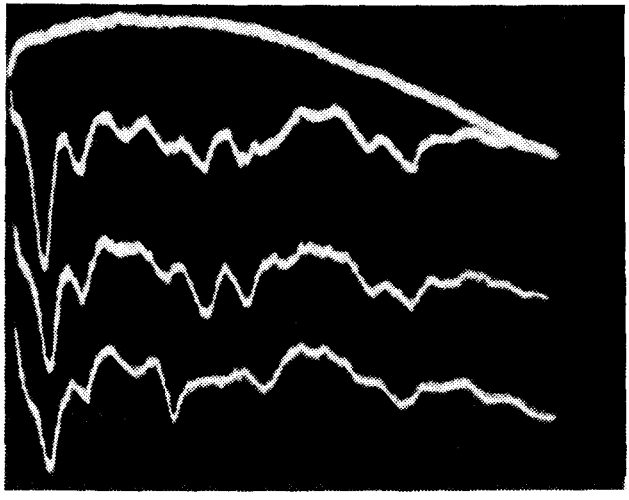
When the ligand hyperfine interaction (HFI) is investigated by electron nuclear ›uble resonance (ENDOR), the signs of the components of the HFI tensor for .e case $S=1/2$ remain unknown. They are usually determined by the method of ·iple electron-nuclear-nuclear resonance (TENNR), which does not always ve the desired results, however.[1,2]



'IG. Oscillograms of ESR line of tetragonal Yb^{3+} center in CaF_2 at $\mathbf{H} \| [001]$, il-ıstrating the selective weakening of the discrete saturation spectra at radio fre-uencies corresponding to splitting of the electron levels by one of the nuclei f the second coordination sphere: 1—section of equilibrium ESR line; 2—dis-rete-saturation spectrum on the same section of the line; 3—attenuation of he system of dips ϵ_- of the discrete-saturation spectrum at the frequency ν_+; —attenuation of the subsystem of dips ϵ_+ of the discrete-saturation spectrum t the frequency ν_-.

We propose in this paper a method of determining the signs of the components of the ligand HFI tensor by radio frequency discrete saturation (RFDS). It is known that pulsed saturation by an ESR line inhomogeneously broadened by surrounding nuclei leads to formation in this line of a discrete saturation (DS) spectrum.[3] When the sample is acted upon simultaneously by microwave and RF pulses, selective resonant attenuation of the intensity of the DS spectrum is observed.[4] For the case of an electron spin $S=1/2$, selective attenuation of the intensity of two subsystems of the DS spectrum take place, at radio frequencies $\nu_{\pm}^{\alpha}$ corresponding to splitting of the electron levels with spin projections $+1/2$ and $-1/2$, produced by the αth nucleus in the surrounding of the magnetic ion.[4] Action at the frequencies ν_{+}^{α}, regardless of the coordination sphere to which the nucleus α belongs, weakens that part of the DS spectrum which corresponds to splittings in levels with electron-spin projection $-1/2$, and vice versa (see the figure). For well-localized paramagnetic centers, the HFI approaches the dipole value even for nuclei of the second coordination sphere, so that it is easy to ascribe the frequencies observed from these nuclei to electronic substates. On the other hand, it is easy to determine the corresponding electronic substate by comparing the character of the action of the frequency from one of the nuclei of the second and more remote coordination spheres with the action of the frequency from any nearest neighbor. By carrying out the measurements in several orientations of the magnetic field relative to the crystal axes it is possible to determine the components of the HFI tensor and their signs.

The proposed method worked well for all the investigated samples, in CaF_2 or SrF_2 with U^{3+}, Yb^{3+}, and Nd^{3+}, in BaF_2 with U^{3+} and Yb^{3+}, and also in $LiIO_3$ in Cr^{3+} and Fe^{3+}.

It was of interest to determine the signs of the parameters of the ligand HFI of Yb^{3+} in CaF_2 in a surrounding of cubic symmetry, which, as noted above, nc could not be done by the TENNR method.[1,2] The signs of the parameters A_s and A_p determined by us for the fluorine nuclei of the first coordination sphere turned out to be positive, as proposed by the authors of[5].

It should be noted that in the RFDS method, owing to the pulsed action of the microwave and RF fields, the relaxation processes do not play any role in a multilevel spin system. It was shown with $CaF_2:Yb^{3+}$ as an example that the method can be successfully used in that case when the TENNR method cannot determine the signs of the HFI parameters.

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