Investigation of the hyperfine interaction of U^{3+} in CaF_2 by the method of radio-frequency discrete saturation

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The method of radio-frequency discrete saturation (simultaneous action of microwave and radio-frequency pulses on the EPR line) we investigated the hyperfine interaction (hfi) of impurity U^{3+} ions with the surrounding fluorine nuclei in CaF_2 single crystals. The hfi tensors were obtained for the nuclei of the first and second coordination spheres, with the accuracy characteristic of the ENDOR method. Small distortions of the crystal lattice, due to the impurity U^{3+} ion, are determined.

In this paper we use, for the first time, the previously observed[1] influence of a radio frequency (RF) field on the discrete-saturation (DS) spectrum as a method of investigating the hyperfine interaction (HFI) of a paramagnetic center with the nuclei surrounding it.

1. Pulsed saturation of a small section of an inhomogeneously broadened EPR line leads, as is well known, to the appearance in this line of a DS spectrum[2,3]. The investigation of such spectra at certain orientations of the magnetic field relative to the crystallographic axes makes it possible to determine the components of the HFI tensor for nuclei in the environment of the magnetic center. Such investigations were carried out for U^{3+} in CaF_2 and SrF_2, where the HFI tensors were determined for eight nuclei of the first coordination sphere[4,5]. The accuracy with which the HFI tensor components were determined by this method was limited by the width of the holes burned in the line and is inferior by more than one order of magnitude to the accuracy typical of the electron nuclear double resonance (ENDOR) method.

We have shown previously[1] that when microwave and radio-frequency pulses act simultaneously on a sample, a resonant weakening of the intensity of the DS spectrum is observed at radio frequencies corresponding to the splitting of the electronic sublevels by the nuclei of the nearest coordination spheres. The width of the resonant action is of the order of the NMR line width in a solid. The attenuation of the intensity of the lines (holes) of the DS spectrum is due to the redistribution of the populations of the electron-nuclear sublevels, on which the saturation of a certain pair of levels, produced by the microwave pulse, is partially lifted by the saturating RF field.

Measurements of the RF field frequencies at which perturbation of the DS spectrum is observed[1)] and, in particular, the attenuation of its intensity, can determine exactly the splitting of the electronic sublevels by the surrounding nuclei, i.e., can yield the same information and with the same accuracy as the ENDOR method. As will be shown below, the experimental procedure and the interpretation of the results are much simpler than in ENDOR. Following Zevin and Brik[6], we use for the aggregate of the effects of the action of the RF field on the DS spectrum a simpler designation, namely radiofrequency discrete saturation (RDS), and the corresponding set of frequencies will be called the RDS spectrum.

2. The investigations were performed with a superheterodyne spectrometer with a third additional klystron for pulsed saturation of the EPR line. The investigated sample was placed at the center of a cavity resonator tuned to the H_{102} mode. The DS spectrum was observed on the screen of an oscilloscope with a driven sweep under pulsed saturation of the EPR line[2]. We used saturating microwave pulses of duration 10-30 μsec and sinusoidal modulation of the magnetic field from the power mains; the modulation extended over the entire EPR line. To obtain a standing picture of the DS spectrum, we used a pulse repetition frequency 50/4 = 12.5 Hz.

The radio-frequency coil was placed in the central part inside the cavity and in the immediate vicinity of its walls. With such a placement of the coil, the Q of the cavity was hardly affected. The RF field was produced in pulses from a GZ-41 generator simultaneously with the microwave pulse. The pulsed action of the RF field, of duration 1-5 msec, makes it possible to increase the power level greatly in comparison with continuous saturation, without producing undesirable effects connected with heating of the sample.

3. We investigated CaF_2 single crystals with 0.1% of U^{3+} as the paramagnetic impurity. In our samples, the magnetic impurity was surrounded by eight F^- ions located at the vertices of a cube, and a ninth F^- ion that compensated for the excess charge of the impurity (see Fig. 1).

It can be shown from symmetry considerations[4,7] that the HFI tensor of the paramagnetic center with nucleus 1 in a coordinate system oriented along the principal axes x, y, z of the cube (see Fig. 1) is given by

$$\hat{A}^1 = \begin{pmatrix} A_1 & A_2 & A_5 \\ A_2 & A_1 & A_5 \\ A_4 & A_4 & A_3 \end{pmatrix}. \tag{1}$$

For the remaining seven fluorine nuclei the HFI tensors

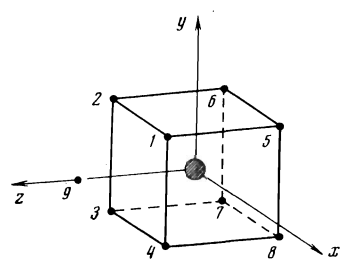

FIG. 1. Model of the immediate vicinity of U^{3+} in single-crystal CaF_2.

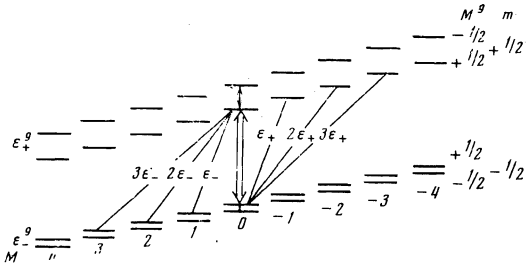

FIG. 2. Electron-nuclear level scheme for the eight equivalent nuclei with allowance for the splitting by the ninth nucleus. The broad arrow shows the saturation of a definite pair of levels by a microwave pulse, the lines designate transitions corresponding to positions of DS holes in the line, while the small arrows mark the RF transitions.

differ in the signs of the components A_2, A_4, and A_5. In addition, it should be noted that, owing to the presence of the ninth fluorine ion, the nuclei 1-4 and 5-8 are not equivalent, i.e., they have HFI tensor components that differ in magnitude.

The ninth fluorine nucleus has a higher symmetry and for this nucleus $A_2 = A_4 = A_5 = 0$, i.e., the HFI tensor is diagonal in the coordinate system x, y, z.

The splittings of the electronic-state levels by the surrounding nuclei $\epsilon_{\pm}^{i}$, where the superscript numbers the nucleus and the subscript pertains to the electronic state $m = +1/2$ or $m = -1/2$, is given by the formula

$$\varepsilon_{\pm}^{i}=[(\hbar\gamma H)^2+{}^1/_4(A_{\parallel}^2+A_{\perp}^2)\mp\hbar\gamma H\bar{A}]^{1/2}, \qquad (2)$$

Here $A_{\parallel}$, $A_{\perp}$, and $\bar{A}$ are HFI parameters whose values are expressed in terms of the components of the tensor $\hat{A}$ and depend on the orientation of the magnetic field relative to the crystallographic axes. For the electronic transitions $-1/2 \leftrightarrow -1/2$, the effective magnetic field acting on the i-th nucleus changes direction in space by an angle χ^i given by the expression[3]

$$\cos\chi^{i}=(\varepsilon_{+}^{i}\varepsilon_{-}^{i})^{-1}[(\hbar\gamma H)^2-{}^1/_4(A_{\parallel}^2+A_{\perp}^2)]. \qquad (3)$$

In these formulas we have left out, for simplicity, the superscript i of the HFI parameters. The probabilities of the forbidden transitions ($\Delta m = \pm 1$, $\Delta M^i = \pm 1$) of the nuclei for which $\cos\chi^i \neq \pm 1$ are of the same order as the probabilities of the allowed transitions ($\Delta m = \pm 1$, $\Delta M^i = 0$).

The investigations were carried out for the following magnetic-field orientations: I–$\mathbf{H}\parallel[001]$; II–$\mathbf{H}\parallel[100]$; III–$\mathbf{H}\parallel[110]$; IV–$\mathbf{H}\parallel[101]$. To determine the components A_1 and A_3 of the tensor of the ninth fluorine nucleus, it suffices to carry out the measurements in the two principal orientations I and II of the magnetic field. At these orientations, the DS spectrum is governed by eight fluorine nuclei. The ninth nucleus makes no contribution to the DS spectrum, since $\cos\chi^9 = \pm 1$.

The level scheme for the eight equivalent nuclei and the level splitting by the ninth nucleus are shown in Fig. 2. Saturation of a definite pair of levels, indicated by the arrow, leads to the formation of a DS spectrum in the EPR line; in the simple case of equivalent nuclei, this spectrum consists of two subsystems of holes, indicated by the oblique lines and separated from the central hole by distances that are multiples of ϵ_+ and ϵ_-. This picture of the DS is obtained, for example, at the orientation $\mathbf{H}\parallel[100]$ for eight almost-equivalent nuclei. At the frequencies $\nu_{\pm}^{9}$ corresponding to the splitting of the levels by the ninth fluorine nucleus $\epsilon_{\pm}^{9}$ the RF field to a selective attenuation of the intensity of one of the subsystems of the observed DS spectrum, namely, ν_{+}^{9} and ν_{-}^{9} cause attenuation of the holes of the subsystem ϵ_- and ϵ_+, respectively. The DS spectrum for nonequivalent nuclei is somewhat more complicated, but the selective action on the holes connected with the upper or the lower electronic states remains in force. Thus, Figure 3 shows oscillograms of the DS spectra in the orientation III, where the DS is due to two pairs of nonequivalent nuclei (1, 3 and 5, 7; the remaining nuclei make no contribution to the DS spectrum), and also shows the different action at the frequencies $\nu_{\pm}^{9}$. The RDS lines connected with the ninth fluorine nucleus can easily be separated from the overall frequency spectrum, because their position has mirror symmetry with respect to the resonant frequency ν_0 of the free fluorine nuclei, and, in addition, the positions of these lines do not change when the sample is rotated around the symmetry axis z.

When the components of the HFI tensor of the nuclei of the first coordination sphere were determined, it was noted that the nuclei that make the main contribution to the DS spectrum ($\cos\chi^i \neq \pm 1$) have weak RDS signals. Moreover, at certain orientations of the magnetic field the RDS due to the nuclei of the first coordination sphere is not observed at all. We note that a similar situation also takes place in the ENDOR method in crystals of the same type[7]. On the other hand, the nuclei that make no contribution to the DS spectrum ($\cos\chi^i = \pm 1$) have intense RDS lines.

A possible cause of the attenuation of the signal is the following: in the case of electronic spin-spin flip-flop reorientations, the nuclei of the first coordination sphere are also rapidly reoriented, owing to the large probability of the forbidden electron-nuclear transitions, and this leads to a decrease of the nuclear time T_{2n} to a value on the order of the electronic time T_{2e}, and consequently to a broadening of the corresponding RDS (ENDOR) signals.

The HFI tensor of the nuclei of the first coordination sphere is determined from measurements of the RDS frequencies in the magnetic-field orientations II, III, and IV. In orientation III, only two equivalent pairs (1, 3 and 5, 7) out of the eight fluorine nuclei govern the DS spectrum (see Fig. 1). For the remaining nuclei (2, 4 and 6, 8) we have $\cos\chi^i = 1$ and intense RDS signals are observed at frequencies that have mirror symmetry with respect to ν_0. These frequencies make it possible

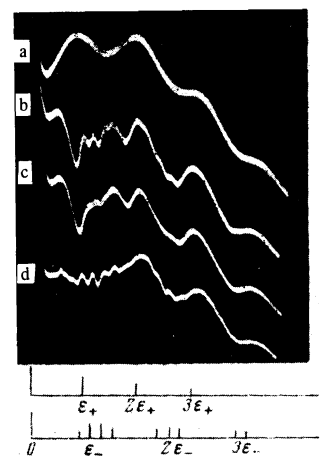

FIG. 3. Oscillograms of EPR line of U^{3+} in CaF_2 in the orientation $\mathbf{H}\parallel[110]$, illustrating the selective attenuation of the DS spectrum at radio frequencies corresponding to the splitting of the levels by the ninth fluorine nucleus: a–section of equillibrium EPR line, b–DS spectrum in the same section of the line, 3–attenuation of the system of ϵ_- dips of the DS spectrum at the frequency $\nu_+^9 = 22.52$ MHz, d–attenuation of the system of ϵ_+ dips of the DS spectrum at the frequency $\nu_-^9 = 5.70$ MHz.

to determine the differences $A_1 - A_2$ directly. In the orientation II, four relatively weak and broadened RDS signals were observed from two groups of equivalent nuclei (1-4 and 5-8). The RDS spectra obtained in orientations II and III make it possible to determine the components A_1, A_2, and A_4.

The tensor components A_3 and A_5 could have been obtained directly from measurements in orientation I, but in this case the RDS signals of the nuclei of the first coordination sphere were not observed. They were therefore determined from measurements in the nonprincipal orientation IV, using the already known values of A_1, A_2, and A_4.

The HFI tensor components could be selected unambiguously by comparing the calculated parameters $\epsilon_{\pm}^{i}$ in different orientations with the observable DS spectra in the corresponding orientations.

The obtained values of the HFI tensors must be correctly ascribed to the nuclei of the groups 1-4 and 5-8. It appears that in this case it is possible to make such a choice by comparing the DS spectra of U^{3+} in CaF_2 with the analogous spectra in SrF_2[5] and BaF_2, where the displacement of U^{3+} relative to the ninth fluorine ion increases as a result of the increase of the lattice parameter. This is accompanied by an increase in the nonequivalence of the nuclei of groups 1-4 and 5-8. It is not difficult to ascribe the obtained HFI tensors to the nuclei 1-4 and 5-8 in the SrF_2 and BaF_2 lattices, namely, the HFI tensor with the smaller components is ascribed to the more remote nuclei 5-8. By comparing the DS spectra in the orientation [110], where the nonequivalence of the nuclei is most strongly pronounced and the DS spectra vary little on going from CaF_2 to SrF_2 and BaF_2, it is possible to assign the obtained values of the tensors correctly to the groups of nuclei 1-4 and 5-8.

The components of the HFI tensors for the nine fluorine nuclei of the nearest environment of U^{3+} are listed in Tables I and II.

4. At all the investigated orientations of the magnetic field, we observed the RDS spectra from the fluorine nuclei of the second and third coordination spheres. The HFI of these nuclei are close in magnitude to the dipole-dipole interaction of pointlike dipoles, and their resonance lines can therefore be identified easily. From symmetry considerations, all the nuclei of the second coordination sphere can be subdivided into two groups: eight fluorine nuclei of type (113), having the same symmetry of the HFI tensor as the nuclei of the (111) type, and 16 fluorine nuclei of the type (311) and (131), which have a lower symmetry.

Experiment reveals a splitting of certain lines of the second coordination sphere, namely lines from nuclei of type (311). This splitting is due to the presence of small distortions of the crystal lattice, which lead to nonequivalence of nuclei of the type (311) and $(31\bar{1})$. It should be noted that the RDS lines from nuclei of the type (113) and $(11\bar{3})$ did not split. The crystal-lattice distortions are due to the fact that the ninth fluorine ion, which compensates for the excess charge of the impurity, shifts the impurity ion U^{3+} in the direction of the positive z axis by an amount δ and repels the eight fluorine ions that surround it[7]. The more remote ions are also displaced, but these displacements should decrease rapidly with increasing distance and can be

TABLE I

A	Measured values, Nuclei 1-4 MHz	Measured values, Nuclei 1-4 Oe	Measured values, Nuclei 5-8 MHz	Measured values, Nuclei 5-8 Oe	Dipole values, nuclei 1-8 MHz	Dipole values, nuclei 1-8 Oe
A_1	−3.87±0.03	−1.48±0.01	−6.26±0.03	−2.40±0.01	0	0
A_2	12.27±0.04	4.70±0.02	9.26±0.04	3.55±0.02	5.25	2.01
A_3	5.0±0.5	1.0±0.1	−0.2±0.3	−0.04±0.06	0	0
A_4	13.89±0.04	5.32±0.02	12.58±0.04	4.82±0.02	5.25	2.01
A_5	25.1±0.3	5.12±0.06	25.8±0.2	5.26±0.04	9.87	2.01

TABLE II

A	Measured values (nucleus 9) MHz	Measured values (nucleus 9) Oe	Dipole values (nucleus 9) MHz	Dipole values (nucleus 9) Oe
A_1	−16.82±0.01	−6.444±0.005	−3.41	−1.30
A_3	59.6±0.2	12.16±0.05	12.78	2.60
$A_{2,4,5}$	0	0	0	0

TABLE III

A	Measured values, MHz	Dipole values, MHz
A_1	−0.48±0.03	−0.50
A_2	0.19±0.04	0.17
A_3	1.85±0.15	1.86
A_4	0.7±0.3	0.53
A_5	0.96±0.08	0.99

neglected. We shall assume that only the nuclei (±1, ±1, 3) are displaced in the second coordination sphere, and that the displacements along the axes x, y, and z are equal and have a value Δ. Allowance for the displacement improves the agreement between the calculated frequencies and the experimentally observed ones. The following values were obtained for the displacements:

$$\delta = 0.16 \pm 0.04 \text{ Å}; \quad \Delta = 0.14 \pm 0.08 \text{ Å}.$$

The errors in the determination of the displacements are due mainly to the contribution of the covalent bond, which is difficult to account for.

For nuclei of the type (113), measurements in the orientations I, II, and III yeilded the 5 components of the HFI tensor listed in Table III. For comparison, the table also gives the calculated values of the HFI tensor components in the pointlike-dipole approximation.

5. As shown above, the RDS method has made it possible to determine the HFI tensors for the nuclei of the first and second coordination spheres, and also small distortions of the crystal lattice, i.e., to obtain the same information as by the ENDOR method in analogous crystals. At the same time, in comparison with the ENDOR, the RDS method has a number of advantages, due to the simplicity of the experimental procedure and the interpretation of the spectrum.

A. The RDS experiments are performed with an ordinary superheterodyne relaxometer with a resonator, so that simultaneous action of the microwave and RF fields can be effected. The spectrometer need not satisfy such stringent requirements as are necessary for the ENDOR spectra with respect to the stabilization of the magnetic field and the microwave-generator frequency.

B. The pulsed character of the action of the microwave and RF fields on the EPR line makes it possible to neglect the relaxation processes that play an important role in the ENDOR method. Consequently, the interpretation of the physical processes that occur in the

complicated multilevel system becomes much simpler. The use of a pulsed radio-frequency field also makes it possible to raise the RF power level greatly without causing undesirable effects connected with heat release.

C. The interpretation of the RDS spectra becomes much simpler because of the selective character of the action of the RF field on the holes connected with the electronic states $m = +1/2$ and $m = -1/2$, and also, most importantly, as a result of the additional information obtained directly from the DS spectrum. It should be noted that the DS spectra have their maximum intensity in those cases when no RDS spectrum due to the nuclei of the first coordination sphere is observed.

Among the shortcomings of the RDS method are its lower sensitivity in comparison with the ENDOR method, resulting from the use of an oscilloscope to record the spectra. In addition, the RDS method yields maximum information only if the DS spectrum is present in the EPR line, but even in those cases when the conditions for the occurrence of the DS spectra are not satisfied[3] and a single hole is burned in the line, the RDS spectra can be determined from the resonant attenuation of the line intensity under the influence of the RF field.

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[1)] As was shown by Zevin and Brik [6], the action of an RF field can lead, in principle, also to the appearance of induced poles and to the enhancement of definite lines in the DS spectrum.

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