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FLUORINE HYPERFINE STRUCTURE OF THE EPR SPECTRA OF U^{3+} *AND* Tb^{3+} *IONS IN* CaF_2

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The fluorine hyperfine structure of the EPR spectra of U^{3+} and Tb^{3+} in sites of tetragonal symmetry in the CaF_2 lattice is investigated. The interaction between the paramagnetic ion and its surroundings is asymmetric and partially includes the second coordination sphere of F^- ions.

THE EPR of trivalent impurities in sites of tetragonal symmetry in the CaF_2 and SrF_2 lattices was described by Bleaney, Lewellyn, and Jones[1] for U^{3+} and Nd^{3+} ions. According to the model they proposed, a trivalent impurity ion M^{3+} substitutes for a lattice cation M^{2+}, with the charge compensated by an extra F^- ion situated in the center of the neighboring cube of F^- ions. The impurity ion M^{3+} is surrounded by eight F^- ions, located on the vertices of a cube (see Fig. 1), and the additional ninth F^- ion creates an axial intracrystalline field, which leads to anisotropy in the g factor. The axes of this field are directed along the axes of the cube of F^- ions, and so there are three unequivalent M^{3+} ions. This model has been confirmed in many EPR investigations (see, for example, [2-4]).

In the work of Bleaney et al.,[1] a complex hfs (hyperfine structure), caused by the F^- ions surrounding the U^{3+}, was observed in certain orientations of the crystal with respect to the magnetic field; however, the spectrum was not explained. The even number of components of the spectrum indicated that the paramagnetic ion was surrounded by an odd number of F^- ions, in confirmation of the proposed model.

In this paper we make an attempt to explain the fluorine hfs of U^{3+} ions in the lattices of CaF_2, SrF_2, and BaF_2, as well as of Tb^{3+} ion in CaF_2, the fluorine hfs of which was observed earlier.[2]

Figures 2a and 2b show the fluorine hfs spectrum of U^{3+} in CaF_2 for directions of the magnetic field parallel and perpendicular to the symmetry axis. In the latter case the pattern is a superposition of the resonance lines of two unequivalent ions. The lines shown in Fig. 2 are observed at the same time, i.e., without rotating the crystal, because of the presence of three unequivalent ions with mutually perpendicular symmetry axes along [100], [010], and [001]. The fluorine hfs of U^{3+} in surroundings of tetragonal symmetry in SrF_2 and BaF_2 are similar; however, the resolution worsens with increase in lattice parameter.

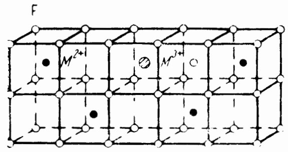

FIG. 1. CaF_2 lattice with a trivalent impurity ion M^{3+} in sites of tetragonal symmetry.

It is known that the hfs of EPR lines due to surrounding nuclei is described by the additional term $\Sigma_n \mathbf{I}^n A^n \mathbf{S}$ in the spin Hamiltonian. Here $\mathbf{S}$ is the effective spin of the electron shell of the paramagnetic ion, in our case equal to 1/2; $\mathbf{I}^n$ is the spin of one of the surrounding nuclei, for F^{19} also equal to 1/2; A is the hyperfine interaction tensor. The summation is taken over all surrounding nuclei.

The expected number of hfs lines when in a specific orientation the hfs constants A_i^n are different for all N surrounding nuclei, is 2^N, and they have the same intensities, which we can conveniently take as unity. In the case of equal A_i^n for all N nuclei, the number of hfs components is N + 1, with a binomial distribution of intensities. In the intermediate case, when the surrounding nuclei can be divided into subgroups with the same A_i^n, the expected number of hfs lines will be intermediate between N + 1 and 2^N with a slow increase in intensity compared with the simple binomial law.

Tinkham[5] has studied the fluorine hfs of some iron-group ions in ZnF_2. He showed that the fluorine hfs constants A_i^n depend strongly on distance; consequently, the observed spectrum is due to the nearest neighbors of the paramagnetic ion. Thus in our case it would be natural to expect the paramagnetic ion to interact with eight or nine ions. The first possibility is contradicted by the even number of observed hfs lines. It can be shown that an interaction with nine F^- ions does not explain the observed spectrum either. In fact, if the total intensity of the individual components (or the aggregate area) is set equal to the number $2^9 = 512$, it can be seen that the outer lines will have an intensity (or area) less than one. In addition, the number of components, 20 and 12, which can be seen on the oscillograph (Fig. 2) does not give a single scheme for grouping the constants $A_{\parallel}^n$ and $A_{\perp}^n$ for nine F^- ions in tetragonal symmetry. Hence, for the additional weaker hfs lines not observable on the oscillograph, the aforementioned contradiction is strengthened. These considerations are even more valid for the case of eight F^- ions.

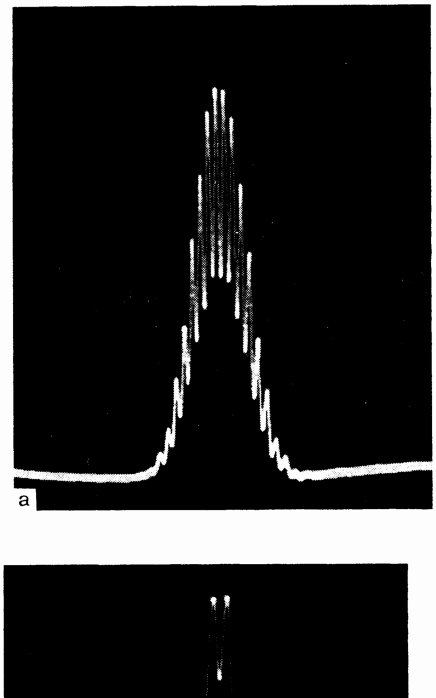

FIG. 2. Fluorine hfs of the EPR spectrum of U^{3+} in CaF_2: a – $H \parallel z$, b – $H \perp z$.

To explain this contradiction we can advance several assumptions. In particular, we can expect a slight distortion of the structure in the vicinity of the impurity center and the appearance of a small rhombic term in the intracrystalline field. This distortion can lead to a slight tilt of the z axis or a change in the g factor. The observed spectrum would then be a superposition of spectra from centers with different forms of distortion. Simple calculation shows that the tilt of the z axis necessary to shift the spectrum by an amount of the same order as the spacing between the hfs components is about 4°, or a shift in g factor equal to $\Delta g \approx 0.01$.

Direct measurements show that any distortion of the structure leading to a tilt of the z axis or a change in g factor is so slight that it cannot give a shift of the spectrum, i.e., a complication of it in the form of superposition. This was shown by measurements of the angular dependence of the line width, as well as by measurements at different frequencies, since the shift of the lines is proportional to the magnetic field in the presence of a Δg. It can also be shown that our spectrum at 9370 Mcs is uncomplicated by the presence of nuclear transitions $\Delta m = \pm 1$, the possibility of which in a certain region of magnetic fields was demonstrated by Clogston et al.,[6] and, in the terminology of these authors, is "simple."

On the basis of this, we can conclude that the number of F^- ions that interact with U^{3+} is greater than nine. The closest F^- ions in the second coordination sphere number 24. Interaction of the paramagnetic ion with the 33 ions of the first and second coordination spheres, even with equal hfs constants for all nuclei, when the intensities vary the fastest, would give a more gradual variation in the intensities in the central (observed) part of the spectrum than is seen in the experiment.

Considering the structure of the surroundings of the paramagnetic ion and keeping in mind that it does not have a center of symmetry, it can be assumed that the paramagnetic ion interacts with 13 F^- ions, partially and asymmetrically embracing the second coordination sphere of F^- ions, consisting of four ions near the axis of symmetry on the side of the extra ion. For an orientation of the magnetic field parallel to the symmetry axis, these 13 ions, in the general case, can obviously be divided into four subgroups (4, 4, 1, 4) with identical constants $A_{\parallel}^n$ in each subgroup ($A_{\parallel}^{1-4}$, $A_{\parallel}^{5-8}$, $A_{\parallel}^{9}$, $A_{\parallel}^{10-13}$).

By calculating the intensities for the multitude of possible ratios of the values of the hfs constants $A_{\parallel}^n$ and by comparing them with the observed spectrum, we have established that to a first approximation the observed spectrum can be described using the ratio $A_{\parallel}^{1-8}/A_{\parallel}^{9-13} = 2$. In this way, the 13 F^- ions divide into two subgroups, each having identical hfs constants, one consisting of the 8 ions forming the cube about the U^{3+}, and the other of 5 ions situated on the same side as the extra F^- ion. The number of hfs components in this scheme is 22 with the following ratio of intensities:

$$1 : 5 : 18 : 50 : 113 : 221 : 376 : 568 : 770 : 938 : 1036.$$

As can be seen in Fig. 3a, the calculated intensities are in good agreement with those observed in the oscillogram of Fig. 2a. They do not, however, reflect one characteristic feature of the spectrum, which can be noted in Fig. 2a and Fig. 3a, namely the non-monotonic variation of intensities, whereby the intensities of neighboring components approach each other in pairs.

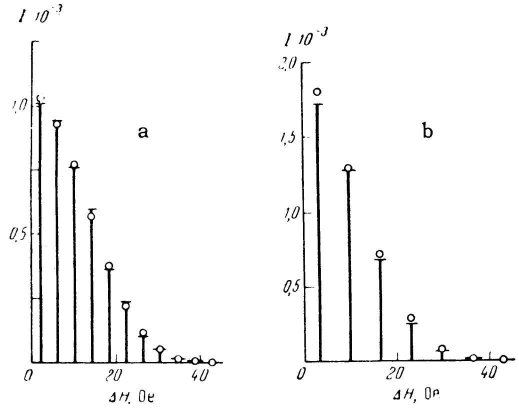

FIG. 3. Intensities of the hfs components, taken respectively from the oscillograms of Fig. 2a and Fig. 2b. The circles are calculated intensities.

It is possible to explain this peculiarity by dividing the second subgroup of five ions into two, consisting of one and four F^- ions. In this approximation, for a small change in the constants $A_{\parallel}^{9} \gtrsim A_{\parallel}^{1-8}/2$ and $A_{\parallel}^{10-13} \lesssim A_{\parallel}^{1-8}/2$, it can be noticed that the hfs lines, while maintaining their equidistant separation, are alternately broadened slightly.

In the orientation with the magnetic field perpendicular to the z axis, the spectrum is described by hfs constants that are the same for all 13 F^- ions. This is a crude approximation, which can be seen if only from the broadening of the lines. Actually, the hfs constants are quite different. However, we determined only the mean value $\bar{A}_{\perp}^{n} = A_{\perp}^{1-13}$ from the spacing between the components. The number of components in this scheme is 14 with a binomial distribution of intensities (Fig. 3b).

Substance	$A_{\parallel}^{1-8}$	$A_{\parallel}^{9}$	$A_{\parallel}^{10-13}$	$\bar{A}_{\perp}^{1-13}$
CaF_2	8.1±0.1	4.3±0.2	3.8±0.2	6.6±0.3
SrF_2	7.6±0.2	3.5±0.2		6.0±0.3
BaF_2	7.2±0.3	3.2±0.3		5.5±0.3

The results of the measurements are presented in the table, where the values of the hfs constants are given in Oersteds.

As was mentioned above, the number of components observable on the oscillograph is 20 and 12 for U^{3+} in CaF_2 (for $H \parallel z$ and $H \perp z$, respectively). According to the proposed scheme the expected number of lines is 22 and 14. Increasing the sensitivity to detect the missing lines by slow sweep of the magnetic field did not produce the desired results, because of the presence on the wings of the line of a group of lines belonging to the hyperfine structure of the isotope U^{235} (nuclear spin 7/2). Actually, the intensities of these lines should be about 10^{-3} times the intensity of the lines from U^{238}, so that they would be just as intense as the line we were seeking.

The fluorine hfs of Tb^{3+} in CaF_2 was observed in[2]. Later, the EPR spectrum of Tb^{3+} in CaF_2 was also studied by Forrester and Hempstead[4]; however, no mention was made of the presence of fluorine hfs in this paper. The lack of resolution is explained by the high concentrations of Tb^{3+} in the samples. The structure is resolved only at concentrations < 10^{-2} % and in the absence of clustering in the monocrystals.

Figure 4 shows the recording of the fluorine hfs of one of the four hfs lines of Tb^{3+} (the nuclear spin of Tb^{159} is 3/2) with the magnetic field parallel to the symmetry axis. The number of lines, equal to 10, and the binomial intensity distribution indicate that the paramagnetic ion interacts with nine ions of the first coordination sphere; however, the equal spacing of the lines, which is hardly probable for an

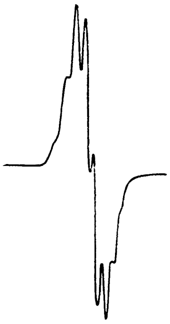

FIG. 4. Fluorine super hfs of one of the four hfs lines of Tb^{3+} in CaF_2.

interaction with nine (8 + 1) F^- ions, as well as the width of the components indicate that the interaction has the same asymmetric character as in U^{3+}. The separation between the components ($A_{||}^{1-9}$) is 2.9 ± 0.2 Oe.

The presence of a significant chemical coupling of a 4f electron with the surroundings for Tb^{3+} can evidently be explained by the fact that in Tb^{3+} there are eight electrons in the 4f shell, which is one more than the seven electrons it takes to half-fill the shell.

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