NUCLEAR MAGNETIC RESONANCE AND HYPERFINE INTERACTION IN CRYSTALS OF THE TYSONITE STRUCTURE

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The magnetic resonance spectra of F^{19} nuclei in CeF_3, PrF_3, NdF_3, and UF_3 polycrystalline samples are studied. The average values of the local magnetic fields near the fluorine nuclei are determined and the values of the hyperfine coupling constants for F^{19} nuclei with the unpaired electrons are estimated. It is shown that the hyperfine interaction constant in CeF_3 is zero, whereas the constant A_π significantly differs from zero in PrF_3, NdF_3, and UF_3. The results obtained are interpreted on the basis of the symmetry properties of the crystals investigated.

It is well known that in certain paramagnetic crystals the unpaired electrons can be delocalized on the adjacent diamagnetic ions. This phenomenon, which is manifested, in particular, in the form of directly induced magnetic fields at the nuclei of the diamagnetic atoms, has been investigated for a number of crystals containing paramagnetic ions with unpaired d-electrons.[1-3]

In this paper we present the results of an investigation of the local magnetic fields appearing as a consequence of the delocalization of unpaired f-electrons in the vicinity of F^{19} nuclei in the trifluorides of Ce, Pr, Nd, and U, which are isostructural with tysonite, LaF_3.[4] The samples of CeF_3 and PrF_3 were obtained by thermal decomposition of NH_4CeF_4 and NH_4PrF_4;[5] they contained less than 1% oxide. The sample of NdF_3 was a commercial reagent of "pure" grade. The UF_3 sample was obtained by reduction of UF_4 by uranium metal;[4] it contained up to 2% UO_2.

For the polycrystalline samples studied (placed in spherical ampules about 8 mm in diameter), the NMR spectra were taken in magnetic fields of from 3 to 9 kOe at temperatures from room temperature to −100 °C (some of the spectra are shown in Fig. 1). The width of the absorption lines (the separation between the points of maximum slope) of the samples is directly proportional to the magnetic field intensity and inversely proportional to $T + \Theta$ (T is the absolute temperature, Θ the Weiss constant). Such behavior and the existence of asymmetry in the spectra are characteristic of paramagnets.

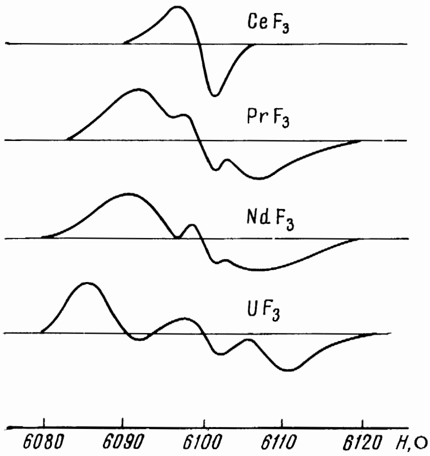

FIG. 1. Derivative NMR spectra of F^{19} in a number of trifluorides at room temperature.

At first sight, the sharp difference in the shape and width of the spectra of CeF_3 on the one hand and the spectra of PrF_3, NdF_3, and UF_3 on the other, is unexpected. To elucidate the source of this difference, the values of the local magnetic fields near the fluorine nuclei were calculated for the tysonite structure. The structure of LaF_3 and its paramagnetic analogs has not yet been completely clarified;[6-8] however, it is known that it can be represented as layers of mutually interpenetrating regular (or almost regular) bipyramids with five fluorine atoms at the vertices and a metal atom Me at the center. In the planes of the layers are arranged three atoms F_I, each of which enters into the composition of three adjacent bipyramids, and above and below the Me atoms on the threefold axes of the crystal there are two atoms F_{II}.

In the lattice there are two F_{II} atoms for every F_I atom.

For simplicity in the calculation we neglected possible small displacements of the Me atoms relative to the three-fold axis, as well as a possible anisotropy of the magnetic susceptibility of the samples studied (the literature contains only values for the susceptibility measured on polycrystalline samples). Under these assumptions, a numerical summation over the entire lattice was accomplished on the "Minsk" computer, and the following total values of the fields due to the dipole moments of the paramagnetic ions near F_I and F_{II} were obtained:

$$H_{F_I} = -0{,}148(3\cos^2\theta - 1)\chi_m H_0(V_{LaF_3}/V_{MeF_3}),$$

$$H_{F_{II}} = 0{,}073(3\cos^2\theta - 1)\chi_m H_0(V_{LaF_3}/V_{MeF_3}).$$

Here χ_m is the molar magnetic susceptibility of the sample, θ is the angle between the direction of the field H_0 and the three-fold crystal axis, $V_{LaF_3}/V_{MeF_3} \approx 1$ is the ratio of the volumes of the elementary cells of LaF_3 and MeF_3.

It is known that the shape and width of NMR spectra are determined by the local magnetic fields near the nuclei.[9] In our case these fields consist of the "electronic" component calculated above and a field-independent nuclear dipole-dipole component (which can be determined from Van Vleck's formula[9]). It is easy to show that without the nuclear component the spectrum of these compounds should be the sum of two components, corresponding to the atoms F_I and F_{II}, with an intensity ratio (ratio of the component areas) of 1:2. The ratio of the width of these components should be 2:1, and the maximum of the more intense component should be shifted toward higher fields and that of the less intense component toward lower fields (see, for example, [10]). Considering the additional broadening of the components due to the nuclear dipole-dipole interaction, one can expect that the total spectrum will be an unresolved asymmetrical line with a shift of the maximum of absorption toward stronger fields (the component associated with the F_I nuclei will be difficult to distinguish because of its greater width and lower intensity).

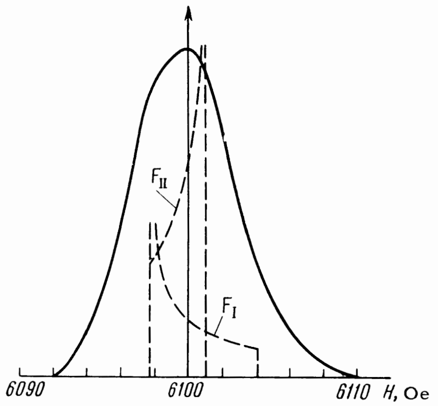

FIG. 2. Calculated line shape of the F^{19} NMR in CeF_3, excluding the internuclear interaction, (dashed line) and the experimental CeF_3 spectrum (solid curve, obtained by numerical integration of the curve in Fig. 1).

As is seen from Fig. 2, the spectrum of CeF_3 corresponds to this picture. This can be seen also by comparing the width of the spectrum with the calculated value. The electronic component of the second moment, determined on the basis of the calculated values of the local fields ($\chi_m = 2.19 \times 10^{-3}$, $H_0 = 6.1$ kOe), is 1.6 Oe^2, and the Van Vleck component is 6 Oe^2. The total value 7.6 Oe^2 agrees with the experimental value 8 ± 1 Oe^2 (for $H_0 = 6.1$ kOe).

At the same time, the spectra of PrF_3, NdF_3, and UF_3 are resolved into two components, but the width of the more intense component, due to the F_{II} nuclei, is not half the width of the other; on the contrary, it is three to six times greater. It is also significant that the maxima of absorption of the more intense components in the spectra of PrF_3, NdF_3, and UF_3 are shifted to lower fields.

The observed difference from the calculated picture can be explained if it is assumed, in accordance with known ideas,[1-3] that in these compounds there is a transfer of unpaired electron density from the metal ions to the F_{II} ions. From the recorded spectra, by using Shulman's method,[1] it is possible to determine the constants of the hyperfine interaction A_{2s}, $A_\sigma - A_\pi$ of the F_{II} nuclei with the unpaired electrons and the spin density of these electrons in the vicinity of F_{II}. Without giving the details of this calculation, we find that for the F_{II} nuclei in NdF_3

$$A_{2s} = 0; \quad A_\sigma - A_\pi = -3.26\cdot 10^{-4}\ \text{cm}^{-1}$$

where the subscripts on A indicate the configuration of the unpaired electrons on F_{II} (see [1]). On the basis of these values, a lower limit was obtained for the density of unpaired electrons near the F_{II} nuclei (assuming $A_\sigma = 0$):

$$f_\pi = 2SA_\pi / A_{2p} = 2.4\%.$$

Here S is the spin of Nd^{3+}, $A_{2p} = 0.0249$ cm^{-1}.[1] The corresponding values for PrF_3 and UF_3 were not calculated because of the lack of some of the necessary data. However, judging from the close similarity of the widths of the spectra, one can expect that for these compounds the values of the spin density near the F_{II} nuclei will also be close.

The result obtained is a direct indication of the participation of the f-shells in the formation of the interatomic bonds in crystals of the tysonite structure. Obviously, the transfer of spin density to the F_{II} atoms cannot occur by using the d-shells of the Me atoms. In this case the spin density near the fluorine ions would be proportional to the population of the d-level. Consequently, one would observe a sharp difference between the spectra of NdF_3 and UF_3, since Nd^{3+} and U^{3+} ions have the same number of f-electrons, but a different spacing between the f- and d-levels.

An analysis of the symmetry of the bonds between the metal atom and the five fluorine atoms in the tysonite structure allows one to understand why the phenomenon of transfer of spin density from Ce^{3+} to the F^- ions is not observed in CeF_3. By comparing the symmetry of the bipyramidal complex MeF_5 (point group D_{3h}) with the symmetry of the atomic orbits of the central ion by Kimball's method,[11] one can readily see that of all the atomic s-, p-, d-, and f-orbitals of the Me atom only one f-orbital cannot participate in the formation of interatomic bonds. Consequently, not more than one unpaired electron in MeF_3 compounds of the tysonite structure can be localized wholly near an Me ion (the electronic configuration of Ce^{3+} is $4f^1$). If the number of unpaired electrons is greater than one, then these electrons of necessity will take up molecular σ- and π-orbitals, and therefore transfer of spin density from Me to F^- ions will be possible.

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