SOVIET PHYSICS JETP VOLUME 29, NUMBER 6 DECEMBER, 1969

SPATIAL DISTRIBUTION OF SPIN DENSITY AND NUCLEAR MAGNETIC RESONANCE IN $RbFeF_3$

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Submitted January 10, 1969

Zh. Eksp. Teor. Fiz. 56, 1823–1832 (June, 1969)

Local magnetic fields at the nuclei of F^{19}, Rb^{87}, and Rb^{85} in $RbFeF_3$ were determined at room temperature by the NMR method. The hyperfine interaction constants were calculated and values of the spin density at these nuclei were determined. It was found that the spin density changed its sign in the space between the fluorine and rubidium nuclei. The values obtained for the spin density at the rubidium nuclei were in good agreement with the theoretical conclusion that the spin density near rubidium was due to the presence of unpaired spins in the t_{2g} orbitals.

THE delocalization of the spin density in paramagnetic crystals gives rise, because of the hyperfine interaction, to local magnetic fields at the nuclei of nominally nonmagnetic ions. Investigations of local fields at the nuclei of various ions make it possible to determine the values of the spin density near these nuclei and to find the spatial distribution of the spin density across a sample. If an experimenter has a batch of crystals, which have similar properties (for example, the same crystal structure, etc.) but differ only in the nature of their paramagnetic ions he can investigate the relationship between the electron configuration of the paramagnetic ions and the nature of the spin density distribution in a crystal.

Such a relationship can be investigated partly in $RbMnF_3$[1,2] and $RbCoF_3$[3] crystals, which have the same structure (of the perovskite type) but different electron configurations of their paramagnetic ions: the ^6S state in Mn^{2+} and the ^4F state in Co^{2+} ions. The hyperfine magnetic fields in these crystals have already been measured, the hyperfine interaction energies have been calculated, and the spin densities at the fluorine and rubidium nuclei have been determined. It has been found experimentally that the spin density at rubidium in $RbCoF_3$ is several times lower than that at rubidium in $RbMnF_3$.

It would be interesting to study also the dependence of the spin density at the nuclei of fluorine in these crystals. The spin density at the fluorine nuclei in perovskite-type crystals is, as shown earlier, due to unpaired spins in the e_g orbitals of paramagnetic ions. Mn^{2+}, Fe^{2+}, and Co^{2+} have the same number of unpaired spins in the e_g orbitals but the average values of the projections of the electron spins in the ground states of these ions are different because of the considerable influence of the spin-orbit interaction in Co^{2+} and Fe^{2+}. Therefore, it would be interesting to study changes in the spin density at the fluorine nuclei, since this should give information about the influence of the spin-orbit interaction on the spatial distribution of the spin density in crystals.

DESCRIPTION OF EXPERIMENTS

The method of preparation of $RbFeF_3$ single crystals and the results of a chemical analysis are reported in[4]. At room temperature, $RbFeF_3$ has the cubic structure of perovskite[5,6] (Fig. 1). Below T = 102°K, this compound transforms to a magnetically ordered state.[1] The sample, on which our measurements were carried out, had a volume of ~0.8 cm³ and consisted of a mosaic of single crystals ranging in volume from 5 to 50 mm³. Since the cubic faceting of single crystals was well developed, a sample prepared this way was quite suitable for measurements of the angular dependences of the NMR spectra of fluorine. The NMR measurements were made with the RYa-2301 unit at room temperature.

The angular dependence of the NMR lines of F^{19}, obtained by varying the angle θ between H_0 and [001] [H_0 lies in the (110) plane], is shown in Fig. 2. The resonance frequency used in the measurements on the fluorine nuclei was $f_0 = 35.258$ MHz. The undisplaced position of the NMR lines of fluorine should be found at a magnetic field $(H_0)_{\text{undispl}} = 8802.4$ Oe. It is evident from Fig. 2 that the positions of the NMR lines were displaced considerably from this value of $(H_0)_{\text{undispl}}$ in the direction of weaker fields. This meant that the fluorine nuclei in a crystal were acted upon by a local

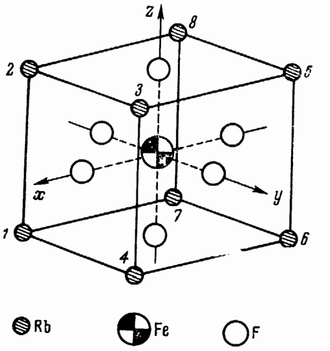

FIG. 1

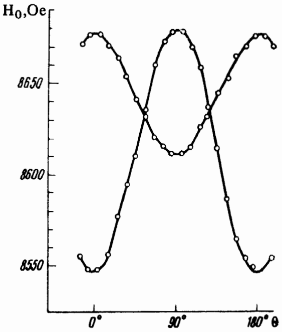

FIG. 2

FIG. 1. Unit cell of $RbFeF_3$. Cubic complex $[FeF_6Rb_8]^{4+}$.

FIG. 2. Angular dependence of the positions of the NMR lines of fluorine in $RbFeF_3$. The two curves represent magnetically inequivalent positions of the fluorine nuclei in the $RbFeF_3$ lattice.

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[1] The transition temperature can be deduced from the disappearance of the NMR signal.

magnetic field directed parallel to the external field. The width of the NMR lines of F^{19} (defined as the separation between the extrema of the derivative) was $\delta H = 13 \pm 1$ Oe.

The measurements on the Rb^{85} nuclei were carried out at a frequency $f_0 = 4.1887$ MHz and those on the Rb^{87} at $f_0 = 12.484$ MHz. In both cases, the lines were shifted in the direction of stronger fields, compared with the positions of the NMR lines of Rb^{85} and Rb^{87} in a standard nonparamagnetic sample, which was an aqueous solution of Rb_2CO_3. These shifts were independent of the angle and their relative value $\alpha = \Delta H/H_0 = (-11.2 \pm 0.7) \times 10^{-4}$ was the same for both isotopes (within the limits of the experimental error). A negative sign was obtained because the local field at rubidium was directed opposite to H_0. The line width for the NMR of Rb^{85} was $\delta H = 7 \pm 1$ Oe and the line width of Rb^{87} was $\delta H = 12 \pm 2$ Oe.

INTERPRETATION OF RESULTS

The observed shifts of the NMR lines are due to the dipole-dipole and hyperfine interactions of the investigated nuclei with paramagnetic ions.

Taking into account the axial tetragonal symmetry of the environment of fluorine, we find that the phenomenological Hamiltonian, describing the Zeeman splittings of the levels of the fluorine nuclei in the paramagnetic state of $RbFeF_3$, is given by

$$\mathscr{H} = -\gamma_F\hbar[H_0 + H^D(3\cos^2\theta - 1)]\hat{I}_z + 2[A_s{}^F + A_p{}^F(3\cos^2\theta - 1)]\langle\langle S_z\rangle\rangle\hat{I}_z. \tag{1}$$

Here, H^D is the amplitude of the dipole magnetic fields exerted on a given fluorine nucleus by the surrounding paramagnetic Fe^{2+} ions, which are regarded as point dipoles; $\hat{I}_z$ is the nuclear spin operator; A_s^F and A_p^F are, respectively, the isotropic and anisotropic hyperfine interaction constants; θ is the angle between the direction of H_0 (the z axis) and the axis joining the fluorine nucleus and an Fe^{2+} ion; the coefficient 2 appears because we are taking into account only the hyperfine interaction with two nearest Fe^{2+} ions; $\langle\langle S_z\rangle\rangle$ is the thermodynamic average value of the z projection of Fe^{2+} spin

$$\langle\langle S_z\rangle\rangle = \frac{\mathrm{Sp}\, S_z \exp(-\mathscr{H}_{Fe}/kT)}{\mathrm{Sp}\exp(-\mathscr{H}_{Fe}/kT)}, \tag{2}$$

where $\mathscr{H}_{Fe}$ is the total electron Hamiltonian of an Fe^{2+} ion, which includes also the exchange interactions; k is the Boltzmann constant.

The rubidium nuclei have a cubic environment consisting of paramagnetic ions. Therefore, the Hamiltonian for these nuclei does not have angular components and is of the form

$$\mathscr{H} = -\gamma_{Rb^r}\hbar H_0\hat{I}_z^{Rb^r} + 8H_s^{Rb^r}\langle\langle S_z\rangle\rangle\hat{I}_z^{Rb^r}. \tag{3}$$

Here, the index r denotes the type of the isotope ($r \equiv 87$ or 85) and the coefficient 8 appears taking into account only the nearest Fe^{2+} ions (there are eight of them).

It follows from Eq. (1) that the NMR frequency of fluorine is given by:

$$f_0{}^F = \frac{\gamma_F}{2\pi}\left\{H_0 + H^D(3\cos^2\theta - 1) - \frac{2[A_s{}^F + A_p(3\cos^2\theta - 1)]}{\gamma_F\hbar}\langle\langle S_z\rangle\rangle\right\}. \tag{4}$$

For the NMR of rubidium, we have

$$f_0^{Rb^r} = \frac{\gamma_{Rb^r}}{2\pi}H_0(1+\alpha) = \frac{\gamma_{Rb^r}}{2\pi}H_0\left[1 - \frac{8A_s^{Rb^r}\langle\langle S_z\rangle\rangle}{\gamma_{Rb^r}H_0\hbar}\right]. \tag{5}$$

We must calculate H^D and $\langle\langle S_z\rangle\rangle$ in order to find the hyperfine interactions constants from the experimental data. The dipole fields in Eq. (1) do not include the contribution of the demagnetizing fields or the Lorentz fields because estimates show that the sum of corrections for these fields is small compared with the fields observed at the nuclei. We shall calculate H^D due to Fe^{2+} ions in a Lorentz sphere using the dipole sums of Shulman and Knox[7] for $KMnF_3$ since $KMnF_3$ has the same structure as $RbFeF_3$ and the dimensions of the unit cells of these two compounds differ only slightly ($a_{KMnF_3} = 4.19$ Å, $a_{RbFeF_3} = 4.173$ Å[5]). Then, we have $H^D = 0.318\chi_m H_0$, where, according to[9], $\chi_m = 8 \times 10^{-3}$. It is more difficult to calculate $\langle\langle S_z\rangle\rangle$.

The energy levels have been calculated by Low and Weger[8] with an accuracy to the second order in the spin-orbit interaction of a single Fe^{2+} ion in a crystalline field of octahedral symmetry. Figure 3 shows the diagram of these levels. Low and Weger give also the form of the wave functions for these states to the zeroth order in the spin-orbit interaction.

The ground state of a free Fe^{2+} ion has a 25-fold (5 × 5) degeneracy if the spin-orbit interaction is not included. A crystal field of octahedral symmetry splits this state into two but the lower level remains 15-fold degenerate. The spin-orbit interaction reduces the degeneracy still further. At room temperature, all 15 levels are populated and therefore all of them must be included in the calculation of $\langle\langle S_z\rangle\rangle$. Moreover, a considerable contribution to $\langle\langle S_z\rangle\rangle$ is made by the corrections to the wave function, which result from mixing of the states by an external magnetic field. These corrections give rise to energy corrections which are quadratic in H_0 and are unimportant in the electron resonance spectra because they shift the levels by the same amount. However, they are important in calculations of the magnetization because they give rise to the Van Vleck paramagnetism. Moreover, we must take into account the exchange interactions.

The exchange interactions will be allowed for within the framework of the molecular field theory, in which the exchange-interaction Hamiltonian for a given paramagnetic ion is of the following well-known form

$$\mathscr{H}_{ex}{}^i = 2\sum_j J_{ij}\langle\langle S_z{}^j\rangle\rangle\hat{S}_z{}^i.$$

Alternately, assuming that all Fe^{2+} ions are located at equivalent sites, we obtain

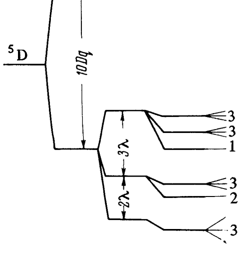

FIG. 3. Energy level diagram of a Fe^{2+} ion: a) free ion; b) splitting in a cubic field of the octahedral symmetry; c) first-order splitting by the spin-orbit interaction; d) second-order splitting by the spin-orbit interaction; e) splitting of levels in an external magnetic field. Numbers show the degree of degeneracy of the levels in the absence of an external magnetic field.

$$\mathscr{H}_{ex}{}^{i} = 2J\langle\!\langle S_z\rangle\!\rangle\hat{S}_z. \tag{6}$$

Here, J is the exchange integral.

Since the energy of interaction of the magnetic moment of a Fe^{2+} ion with the external magnetic field and the energy of the exchange interaction in the paramagnetic state are both much smaller than the energy of the spin-orbit interaction, we can calculate corrections to the wave functions using the perturbation theory and the following perturbation Hamiltonian:

$$\mathscr{H}' = \beta H_0(L_z + 2S_z) + 2J\langle\!\langle S_z\rangle\!\rangle S_z. \tag{7}$$

Here, β is the Bohr magneton ($\beta > 0$); $\hat{L}_z$ is the orbital moment operator. The total Hamiltonian $\mathscr{H}_{Fe}$, used in Eq. (2), includes $\mathscr{H}_Q + \mathscr{H}_{LS} + \mathscr{H}'$, where $\mathscr{H}_Q$ describes the splitting of the Fe^{2+} levels by the crystal field and $\mathscr{H}_{LS}$ describes the spin-orbit interaction.

Using the wave functions found by Low and Weger and calculating corrections to these functions due to the perturbation (7), we obtain

$$\langle\!\langle S_z\rangle\!\rangle = -\beta H\left[\frac{d}{kT(B - 2Jp/\lambda) + 2mJ} - \frac{v}{\lambda}\,\frac{1}{B + 2J(m/kT + p/\lambda)}\right],$$

where

$$d = \frac{21}{2} + \frac{5}{2}e^{2\lambda/kT} + \frac{10}{3}e^{5\lambda/kT}, \qquad v = \frac{18}{5} + \frac{55}{18}e^{2\lambda/kT} - \frac{68}{9}e^{5\lambda/kT};$$

$$P = \frac{6}{5} + \frac{95}{54}e^{2\lambda/kT} - \frac{100}{27}e^{5\lambda/kT}, \qquad m = \frac{9}{2} + \frac{25}{18}e^{2\lambda/kT} + \frac{20}{9}e^{5\lambda/kT},$$

$$B = 3 + 5e^{2\lambda/kT} + 7e^{5\lambda/kT}, \tag{8}$$

and $\lambda = -100\ cm^{-1}$ is the spin-orbit interaction constant.[8]

The susceptibility is calculated in a similar manner and the data on χ_m at T = 298°K can be used to determine the exchange integral. It is found that J/k = 25 deg K.

The value obtained in this case is not very accurate and is essentially an estimate. However, we should bear in mind that the measurements are carried out at temperatures sufficiently high compared with T_N, that $\langle\!\langle S_z\rangle\!\rangle$ depends weakly on J, and that an error of 50% in the determination of J gives rise to an error of only 10–15% in $\langle\!\langle S_z\rangle\!\rangle$.

Calculations yield $\langle\!\langle S_z\rangle\!\rangle = -6.5 \times 10^{-7} H_0$ at room temperature. After the calculation of H^D and $\langle\!\langle S_z\rangle\!\rangle$, the hyperfine interaction constants are determined:

$$A_s{}^F = (20 \pm 1)\cdot 10^{-4}\ cm^{-1} \quad A_p{}^F = (2.5 \pm 0.2)\cdot 10^{-4}\ cm^{-1}$$
$$A_s^{Rb^{85}} = (-2.9 \pm 0.3)\cdot 10^{-6}\ cm^{-1} \quad A_s^{Rb^{87}} = (-10 \pm 1)\cdot 10^{-6}\ cm^{-1} \tag{9}$$

The errors given above are the experimental errors which do not include inaccuracies associated with the various assumptions made in the calculation H^D and $\langle\!\langle S_z\rangle\!\rangle$.

CALCULATION OF THE SPIN DENSITY

The appearance of hyperfine fields at the nuclei of nonmagnetic ions is attributed to the decompensation (polarization) of closed electron shells of these ions because of their interaction with unpaired electron spins of paramagnetic ions. The value of the field at a nucleus is proportional to the degree of decompensation. The quantity which represents the degree of decompensation is the spin density (f_S) at a nucleus may be related to the energy of the contact hyperfine interaction by the following expression:[9,3]

$$f_S = \frac{\langle \mathscr{H}_{cr}^{HFI}\rangle}{\langle \mathscr{H}_{ion}^{HFI}\rangle} = \frac{\langle A_s\hat{I}_z\hat{S}_z\rangle}{\langle a_s\hat{I}_z\hat{S}_z'\rangle} = \frac{A_s\langle S_z\rangle}{{}^1\!/_2 a_s}, \tag{10}$$

where $\mathscr{H}_{cr}^{HFI}$ is the energy of the contact hyperfine interaction in a crystal for a paramagnetic ion in the ground state and with the maximum projection of the magnetic moment along the magnetic field; $\langle S_z\rangle$ is the quantum-mechanical average value of the spin of a paramagnetic ion in this state. We note that, in the case of ions whose orbital moment is not "frozen," the value of $\langle S_z'\rangle$ is not equal to the maximum projection of the spin. The quantity A_s is the hyperfine interaction constant defined in Eq. (1); $\mathscr{H}_{ion}^{HFI}$ is the energy of the hyperfine interaction between a nucleus and one of electrons in the shell of a free nonmagnetic ion, namely, in the shell whose decompensation is responsible for the field at the nucleus; a_s is the hyperfine interaction constant for one electron (with $\langle S_z'\rangle = 1/2$) in that shell.

The wave functions of the ground-state triplet of an Fe^{2+} ion, written in the L_z, S_z representation (for L = 2 and S = 2), are of the form[8]

$$|a\rangle = \left(\frac{3}{20}\right)^{1/2}[|2.1\rangle + |-2,1\rangle + 2|1,2\rangle] + \left(\frac{1}{10}\right)^{1/2}|-1.0\rangle,$$
$$|b\rangle = \left(\frac{3}{20}\right)^{1/2}[|-1,-1\rangle + |1.1\rangle] + \left(\frac{1}{5}\right)^{1/2}[|-2,0\rangle + |2,0\rangle], \tag{11}$$
$$|c\rangle = \left(\frac{3}{20}\right)^{1/2}[|-2,-1\rangle + |2,-1\rangle + 2|-1,-2\rangle] + \left(\frac{1}{10}\right)^{1/2}|1,0\rangle.$$

Here, $|i, k\rangle$ is the wave function of the state with $L_z = i$ and $S_z = k$. Thus, for the $|a\rangle$ state, we have $S_z = 3/2$. We shall now assume that the field at the fluorine nuclei is due to the decompensation of the outer 2s shell (corrections to f_S due to the inclusion of the 1s shells of fluorine are calculated in[10]) and we shall use $a_{2S} = 1.503\ cm^{-1}$ for fluorine.[11] It is natural to assume that, in the case of Rb^+ ions, the field at the rubidium nuclei is mainly due to the decompensation of the outer 5s shell, for which we have[12]

$$a_{5s}^{Rb^{85}} = 0.03376\ cm^{-1} \quad a_{5s}^{Rb^{87}} = 0.11399\ cm^{-1}$$

Then, substituting into Eq. (10) the values of A_S^F and A_X^{Rb}, found from the experimental data, we obtain

$$f_S^F = 0{,}4\,\%, \quad f_S^{Rb} = f_S^{Rb^{85}} = f_S^{Rb^{87}} = -0{,}028\,\%. \tag{12}$$

It is interesting to note that the signs of the spin density at the fluorine and rubidium nuclei are opposite.

We shall continue this analysis mainly to find the relationship between the value of the spin density (hyperfine interaction) at the nuclei of fluorine and rubidium, on the one hand, and the nature of the electron structure of Fe^{2+} ions, on the other. To obtain this relationship, we must calculate theoretically $\langle \mathscr{H}_{cr}^{HFI}\rangle$, i.e., we must obtain an expression for the phenomenological constants A_S^F and A_S^{Rb} in terms of microscopic parameters of electrons, such as the covalence, overlap of the wave functions, and the occupation numbers. We shall consider primarily the hyperfine interaction of the rubidium nuclei, because calculations of the hyperfine interactions of the fluorine nuclei in crystals containing Fe^{2+} ions in the octahedral coordination have been analyzed in detail in[13].

The Hamiltonian of the contact hyperfine interaction is of the form

$$\mathcal{H}_{\rm cr}^{\rm HFI} = \frac{8\pi}{3}\gamma_{\rm Rb}\gamma_e\hbar^2\sum_i \delta(\mathbf{r}_i)\hat{S}_i\hat{I}^{\rm Rb}. \qquad (13)$$

Here, the summation is carried out over all electrons of the system; $\hat{S}_i$ is the spin operator of an i-th electron; $\mathbf{r}_i$ is the radius vector joining an i-th electron and the rubidium nucleus (the origin of the coordinates is assumed to be at the rubidium nucleus); γ_e is the gyromagnetic ratio of the electron. In order to calculate the energy of the hyperfine interaction, we must find the form of the wave function of the many-electron system of interest to us, by expressing it in terms of one-electron functions. The following calculation procedure can be used for this purpose in the weak crystal field approximation.

We shall consider a cubic complex $[\mathrm{FeF_6Rb_8}]^{4+}$, which is shown in Fig. 1. We must express the many-electron functions of Eq. (11) for the ground-state triplet in terms of determinants of the one-electron 3d functions of a paramagnetic ion, and then we must include (for example, by the method of molecular orbitals) the admixture of 2s and 2p functions of fluorine ions, as well as the admixture of the 5s functions of rubidium ions to the one-electron 3d functions of $\mathrm{Fe^{2+}}$ ions. Consequently, the many-electron state is expressed in terms of determinants of the molecular orbitals, including the fluorine and rubidium functions. The energy of the hyperfine interaction of interest to us is expressed by the "mixing" parameters: the covalence and the overlap integrals. It is convenient to classify the one-electron functions of a crystal using the same irreducible representations to which these functions belong in the corresponding symmetry group of the environment. We find that in the octahedral group the 3d functions belong to the e_g ($3d_{x^2-y^2}$ and $3d_{3z^2-r^2}$) and t_{2g} ($3d_{xy}$, $3d_{xz}$, $3d_{yz}$) representations. The expression for the functions (11) in terms of the one-electron 3d functions of $\mathrm{Fe^{2+}}$ can be found in[14]. Our problem is to go over from the "pure" 3d functions to the molecular orbitals, which also include—in addition to the 3d orbitals of $\mathrm{Fe^{+}}$—the functions for fluorine and rubidium, which are transformed in accordance with the e_g and t_{2g} irreducible representations. The general form of these molecular orbitals is as follows:

$$\psi_{\rm MO} = N^{-1/2}\Big(\psi_{3d} + \lambda\sum_i c_i\psi_{\rm F} + \gamma\sum_j \eta_j\psi_{\rm Rb}\Big), \qquad (14)$$

where ψ_{3d} is any one of the five 3d functions. The sums which follow this function are linear combinations of the corresponding orbitals of fluorine and rubidium (i and j are the numbers of fluorine and rubidium ions in the complex $[\mathrm{FeF_6Rb_8}]^{4+}$) and these linear combinations should be transformed in the octahedral group in exactly the same way as ψ_{3d}. We shall consider only the antibonding molecular orbitals. The coefficients λ and γ include the overlap integrals and the covalence parameters. The explicit form of the linear combination of the fluorine functions is well known[11] and we shall not give it here. An elementary group-theoretic analysis shows that there are no combinations of the rubidium 5s orbitals in this complex which could be transformed in accordance with the e_g representation, i.e., there is no overlap or covalence between the $3d_{3z^2-r^2}$ and $3d_{x^2-r^2}$ electrons of $\mathrm{Fe^{2+}}$, on the one hand, and the 5s electrons of rubidium, on the other. However, combinations of the 5s orbitals of rubidium, which are transformed in accordance with the t_{2g} representation, can be obtained[3] and are given by

$$\begin{aligned}\Big(\sum_j \eta_j\psi_{5s}\Big)_{xy} &= \frac{1}{\sqrt{8}}[(\varphi_1+\varphi_5)+(\varphi_2+\varphi_6)-(\varphi_3+\varphi_7)-(\varphi_4+\varphi_8)],\\ \Big(\sum_j \eta_j\psi_{5s}\Big)_{yz} &= \frac{1}{\sqrt{8}}[(\varphi_1+\varphi_5)-(\varphi_2+\varphi_6)-(\varphi_3+\varphi_7)-(\varphi_4+\varphi_8)],\\ \Big(\sum_j \eta_j\psi_{5s}\Big)_{xz} &= \frac{1}{\sqrt{8}}[(\varphi_1+\varphi_5)-(\varphi_2+\varphi_6)-(\varphi_3+\varphi_7)-(\varphi_4+\varphi_8)],\end{aligned} \qquad (15)$$

where φ_j represents the 5s functions of a j-th rubidium atom.

Substituting now Eq. (15) in Eq. (14) and then Eq. (14) into the corresponding determinants, we can show that[2]

$$\begin{aligned}\langle a|\mathcal{H}_{\rm cr}^{\rm HFI}|a\rangle &= \frac{8\pi}{3}\gamma_{\rm Rb}\gamma_e\hbar^2|\psi_{5s}(0)|^2\frac{N^{-1}\gamma^2}{8}n_{t_{2g}}\frac{\langle S_z\rangle}{n}I_z^{\rm Rb}\\ &= a_{5s}\frac{N^{-1}\gamma^2}{8}n_{t_{2g}}\frac{\langle S_z\rangle}{n}I_z^{\rm Rb} = \frac{3}{4}a_{5s}\frac{N^{-1}\gamma^2}{8}I_z^{\rm Rb},\end{aligned} \qquad (16)$$

where n is the number of unpaired spins in a $\mathrm{Fe^{2+}}$ ion and $n_{t_{2g}}$ is the number of such spins in the t_{2g} orbitals.

Comparing Eqs. (10) and (16), we find that

$$f_s^{\rm Rb} = \frac{3}{2}\cdot\frac{N^{-1}\gamma^2}{8}. \qquad (17)$$

A calculation of the contact hyperfine interaction of the fluorine nuclei, given in[13], yields

$$\langle a|\mathcal{H}_{\rm cr}^{\rm HFI}|a\rangle = \frac{1}{2}a_{2s}\frac{N_e^{-1}\lambda_s^2}{3}n_{e_g}\frac{\langle S_z\rangle}{n}I_z^{\rm F} \qquad (18)$$

and it follows from Eq. (10) that

$$f_s^{\rm F} = \frac{3}{4}\frac{N_e^{-1}\lambda_s^2}{3}. \qquad (19)$$

Here, $n_{e_g} = 2$ is the number of unpaired spins in the e_g orbitals; N_e and λ_s are the coefficients, which are similar to N and λ in Eq. (14), but they apply to the molecular orbitals which transform in accordance with the e_g representation.

In these calculations, we have ignored cross terms, which include products of the fluorine and rubidium functions, assuming that they make contributions of higher orders of smallness.

DISCUSSION

The experimental values obtained for the spin densities at the fluorine and rubidium nuclei show that $\mathrm{RbFeF_3}$ exhibits an experimentally observable delocalization of the spin density and this delocalization can be determined for all the nuclei of nonmagnetic ions. It is interesting to note a reversal of the sign of the spin density on going over from the fluorine to the rubidium nuclei, i.e., the presence of spatial oscillations of the spin density which is analogous to the effect observed in $\mathrm{RbCoF_3}$ and $\mathrm{RbMnF_3}$. The appearance in this case of a negative sign of the spin density is difficult to explain because the analysis includes only the antibonding molecular orbitals. However, it is reported in[15] that, in the simpler case of $\mathrm{RbMnF_3}$, in which paramagnetic ions are in the s state and therefore calculations are easier, the

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[2] Calculations of this type are described in greater detail in [3,13].

negative sign of the spin density at Rb may be due to the influence of electrons at filled t_{2g} molecular orbitals of the bonding type. Then, the parameter $N^{-1}\gamma^2$ is replaced by the difference $(N^{-1}\gamma^2) = (N^{-1}\gamma^2)^S_{\uparrow} - (N^{-1}\gamma^2)^S_{\leftarrow}$, where the arrows indicate the directions of spins in the antibonding and bonding orbitals. In this case, we can have, in principle, a negative value of the spin density.

Calculations given in the present paper and in[3] show that the hyperfine interaction and, consequently, the absolute value of the spin density at the rubidium nuclei are both proportional to the factor $n_{t_{2g}}\langle S_z\rangle/n$.

Figure 4 shows the occupation diagram of the 3d electron shell of paramagnetic ions. Bearing in mind that the quantity $\langle S_z\rangle$ is equal to 5/2 for Mn^{2+}, 5/6 for Co^{2+}, and 3/2 for Fe^{2+}, we can easily obtain the following ratio:

$$f^{Rb}_{S(RbMnF_3)}:f^{Rb}_{S(RbFeF_3)}:f^{Rb}_{S(RbCoF_3)} = 1:0.5:0{,}2,$$

if the parameter $N^{-1}\gamma^2/8$, which depends on the interatomic distances and on the covalence, is the same for these crystals. The experimentally determined values of f^{Rb}_S are related by the ratio 1 : 0.51 : 0.26.

It is interesting also to compare the spin densities at the fluorine nuclei. For all three crystals, the number of unpaired electrons in the e_g orbitals is the same but the values of $\langle S_z\rangle$ are different and therefore we should have:

$$f^{F}_{S(RbMnF_3)}:f^{F}_{S(RbFeF_3)}:f^{F}_{S(RbCoF_3)} = 1:0{,}75:0{,}555.$$

The experimentally obtained ratio is 1 : 0.77 : 0.40.

The agreement between the calculated and observed ratios supports our main conclusion that the spin density at the rubidium nuclei is solely due to unpaired spins in the t_{2g} orbitals and the spin density at the fluorine nuclei is solely due to unpaired spins in the e_g orbitals. Since we have compared the ratios of the spin densities, our conclusion is independent of the definition of the spin density (which is associated in this paper with the value of the decompensation of any one electron shell). Basically, this conclusion follows from a direct comparison of the calculated and experimental values of the hyperfine interaction energies $\mathcal{H}^{HFI}_{cr}$ for the crystals discussed.

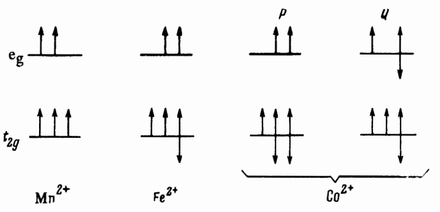

FIG. 4. Occupation diagram of the e_g and t_{2g} orbitals for Mn^{2+}, Fe^{2+}, Co^{2+} ions in an octahedral environment. The ground state of Co^{2+} is the superposition of the P and Q states, where $P^2 \approx 0.9$ and $Q^2 \approx 0.1$.

The author is grateful to G. A. Smolenskiĭ for his interest in this investigation; to G. M. Nedlin for reading the manuscript and discussing the results of the calculations; to V. F. Korneev for his help in the measurements; and to P. P. Syrnikov for the preparation of single crystals.

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Translated by A. Tybulewicz
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