Contribution of the higher magnetic multipole moments of the Tm³⁺ ions to the local field at the ¹⁹F nuclei and the indirect spin-spin interaction in the LiTmF₄ crystal

M. V. Eremin, I. S. Konov, and M. A. Teplov

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It has been established by means of investigations of the magnetic resonance of the ¹⁹F nuclei in the Van Vleck paramagnet LiTmF₄ that the local magnetic field at the fluorine nuclei is not proportional to the paramagnetic susceptibility of the crystal. An analysis of the interionic interactions is carried out, and the existence in the thulium-fluorine interaction Hamiltonian of new, previously neglected operator forms is inferred. It has been experimentally demonstrated for the first time that, owing to the Pauli exchange forces, the higher magnetic multipole moments can make a significant contribution to the paramagnetic ion-ligand interaction energy. An anisotropic indirect interaction between the nuclear spins of ¹⁶⁹Tm and ¹⁹F has been discovered which is by far stronger than the dipole-dipole interaction.

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Paramagnetic ions with an even number of electrons in the unfilled shell can have a nondegenerate (singlet) ground state in the crystal electric field. Substances containing ions with a singlet ground state are called polarizing, or Van Vleck, paramagnets. It is well known that, in the absence of a constant magnetic field, an ion in the singlet state does not possess a permanent magnetic moment. An applied magnetic field *H* admixes into the ground state the wave functions of the excited states, and induces a dipole magnetic moment:

 $\mu = \chi_{V-V}^{\text{ion}} H. \tag{1}$

Here χ_{v-v}^{ion} is the Van Vleck susceptibility per ion. In some praseodymium and thulium compounds the magnetic moments (1) of the Pr^{3+} and Tm^{3+} ions attain, in fields of the order of 10,000 G, values of tenths of a Bohr magneton, and therefore produce high local magnetic fields at the diamagnetic ions surrounding them. By investigating the magnetic resonance of the nuclei of the diamagnetic ions, we can obtain information about the crystal structure of the substance, the interatomic distances, the electronic states of the paramagnetic ions, etc. The interpretation of the results of such experiments is especially simple if the paramagnetic ions and the nuclear moments of the diamagnetic atoms are coupled only through the magnetic dipole-dipole interaction. In the majority of the dielectric Van Vleck paramagnets the dipole-dipole interaction predominates; therefore, it might have been expected that the local magnetic fields produced by the paramagnetic ions at the ligand nuclei would turn out to be simply proportional to the paramagnetic susceptibility of the substance. In the present paper we report the results of experiments on the Van Vleck paramagnet LiTmF₄ which have revealed a deviation from the above-indicated proportionality, carry out a rigorous analysis of the interionic interactions, and deduce the existence in the paramagnetic ionligand interaction Hamiltonian of new, previously neglected operator forms. The observed fine structure of the NMR lines of ¹⁹F is explained by an indirect interaction between the nuclear moments of thulium and fluorine via the electron shells of these ions.

The double fluoride $LiTmF_4$ has the crystal structure of the sheelite CaWO₄ with lattice constants $a_0 = 5.15$ Å and $c_0 = 10.64 \text{ Å}^{[1]}$; the point group symmetry of the environment of the rare-earth ion is S_4 . The nearest neighborhood of the Tm³⁺ ion is formed by eight F ions (Fig. 1). An investigation of the magnetic resonance of the ¹⁶⁹Tm nuclei showed^[2] that the magnetic properties of LiTmF₄ in the temperature range 1.6-25 K are determined by the lowest three states of the Tm³⁺ ion in the crystal field: the ground singlet $|0\rangle$ and the excited doublet $|d\rangle$ and singlet $|s\rangle$ with energies Δ_d and Δ_s . The intracrystalline-electric-field potential of $LiTmF_4$ is unknown. However, we can expect it to differ little from the crystalline potential proposed by Tenssen et al. in Ref. 3 for the Tm^{3+} ion in the LiYF₄ lattice, and can use in the subsequent computations the wave functions found on the basis of that potential.^[3]

The NMR spectra of ¹⁹F (spin $I = \frac{1}{2}$) were investigated at temperatures of from 1.6 to 25 K in a magnetic field of the order of 5,000 G directed perpendicular to the



FIG. 1. The structure of the immediate environment of the Tm^{3+} ion in the LiTmF₄ crystal: the heavy small circle denotes the central Tm^{3+} ion, o) the F⁻ ions; the symbols F₁ and F₂ designate the positions of the fluorine ions located respectively at distances 2.33 and 2.42 Å from the thulium ion.



FIG. 2. Angular dependence of the local magnetic fields produced by the Tm³⁺ ions at the fluorine nuclei in the F₁ and F₂ positions; the external magnetic field is perpendicular to the crystallographic axis c; H_0 is the resonance magnetic field of the "free" fluorine nuclei; φ is the angle defining the direction of the constant magnetic field in the *ab* plane; the dashed curve was computed from the formula (3), the continuous curve was computed from the formula (9), •) experiment.

crystallographic axis c. The magnetic moment of the Tm^{3+} ion and, consequently, the local fields at the ¹⁹F nuclei have maximum values for such an orientation of the crystal.^[2] The F^- ions in the LiTmF₄ lattice occupy two nonequivalent sites: F_1 and F_2 (their distances to the nearest thulium ion are equal to $R_1 = 2.33$ Å and $R_2 = 2.42$ Å), and, accordingly, there are observed in the transverse magnetic field two NMR lines of ¹⁹F whose positions depend on the orientation (the angle φ) of the magnetic field relative to the crystallographic axes a and b. In Fig. 2 the points represent the results of the measurements, while the dashed lines are the computed curves, obtained under the assumption that the splitting of the NMR lines of ¹⁹F owes its origin to the thulium-fluorine magnetic dipole-dipole interaction. The large discrepancy between the computed and measured curves forced us to conjecture that the thulium ions and the fluorine nuclei are coupled not only via the dipole-dipole interaction. This supposition was corroborated in the study of the temperature dependence of the local magnetic fields at the fluorine nuclei: it was observed (Fig. 3) that, as the temperature was raised, the local field decreased more rapidly than the paramagnetic susceptibility of the crystal. The shapes of the curves in Fig. 3 attest to the presence between the thulium ions and the fluorine nuclei of some additional interaction, whose influence on the deviation, δ , of the curves is the greater, the more populated the excited doublet $|d\rangle$ turns out to be.

There arises the question of the nature of this interaction: Does it not arise as a result of the overlap of the electron orbits of the thulium and fluorine ions? It is well known that the partial collectivization of the electrons in a paramagnetic ion A-ligand B system decreases the magnitude of the orbital moment $\ensuremath{^{[4]}}$ and also gives rise to an isotropic interaction of the type $A_{\rm s}S_{\rm A}I_{\rm B}$.^[5] It is, however, not difficult to verify that these effects cannot lead to a difference between the temperature dependences of the paramagnetic susceptibility of the crystal and the local magnetic fields at the fluorine nuclei. Since there do not exist in the thuliumfluorine pair any other types of interactions that are linear in the total moment J, it is natural to suppose that the higher multipole magnetic moments of the Tm³⁺ ion should be responsible for the sought-for interaction.

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FIG. 3. Nonproportionality of the local magnetic field at the ¹⁹F nuclei to the paramagnetic susceptibility of LiTmF₄. The continuous curve is a plot of $\chi(T)/\chi(0)$; the dashed curve, of $H_{10c}(T)/H_{10c}(0)$.

This assumption is easy to verify. The magnetic fields produced by the multipole moments of thulium at the fluorine nuclei should reflect the symmetry of the immediate neighborhood of the paramagnetic ion, and, consequently, in the tetragonal crystal LiTmF₄ (Fig. 1) the angular dependence of the deviation, $\delta = \delta(\varphi)$ should have the form of a four-leaved rosette. Measurements of the quantity δ , which were performed at a temperature of 12.6 K, showed that such type of angular dependence does indeed obtain (Fig. 4), and that the cause of the anomalous temperature dependence of the local magnetic field at the ¹⁹F nuclei may be the induced multipole moments of the thulium ion.

The local field produced by the multipole moments of the thulium ions at a fluorine nucleus can be conditionally split up into two components: a direct and an exchange component. Only the spatial distribution of the electrons of the unfilled shell of thulium is responsible for the direct local field, whereas the exchange field is due to the Pauli forces acting in the overlap region of the electron orbits of thulium and fluorine.

We take the direct local fields at the fluorine nuclei into account by expanding the electron-nucleus interaction Hamiltonian

$$\mathscr{H}=2\beta\gamma\hbar\mathbf{I}_{s}\left\{\frac{\mathbf{I}_{s}}{r_{s}^{3}}-\frac{\mathbf{s}}{r_{s}^{2}}+3\frac{\mathbf{r}_{s}(\mathbf{s}\mathbf{r}_{s})}{r_{s}^{3}}+\frac{8\pi}{3}\mathbf{s}\delta(\mathbf{r}_{s})\right\}$$
(2)

in a series in powers of r_A/R (*R* is the distance between the thulium and fluorine ions). Such an expansion has been carried out by Johnston^[6]; it can be represented in a form consisting of two parts: a dipole-dipole part



FIG. 4. Angular dependence of the deviation from each other of the $H_{1oc}(T)/H_{1oc}(0)$ and $\chi(T)/\chi(0)$ curves measured at T= 12.6 K in a magnetic field $H \perp c$; the zero of the angle φ corresponds to the equality of the local fields at the F₁ and F₂ locations; the continuous curve is a theoretical curve computed from the formula (9), •) experiment.

and a part describing the interaction of the higher multipole moments of thulium with the nuclear moments of fluorine. Combining only the dipole-dipole part with the Zeeman interaction Hamiltonian $g\beta$ H·J in second-order perturbation theory, and summing over all the thulium ions, we obtain a formula for the computation of the local field produced at a fluorine nucleus by the dipole magnetic moments of the ions:

$$\begin{array}{l} 10^{3}H_{\rm loc}^{\rm up} / H_{\rm s} = 2.40\lambda_{\rm t} + 2.87\lambda_{\rm 2} \pm (3.25\lambda_{\rm t} + 3.87\lambda_{\rm 2})\cos 2\varphi \\ \mp (16.10\lambda_{\rm t} + 19.20\lambda_{\rm 2})\sin 2\varphi \end{array} \tag{3}$$

(the dashed line in Fig. 2). In the formula (3) and below we use the notation: φ is the angle between the crystallographic axis and the direction of the external magnetic field,

$$\lambda_{1} = \frac{1 - \exp(-\Delta_{d}/kT)}{1 + 2\exp(-\Delta_{d}/kT) + \exp(-\Delta_{s}/kT)},$$

$$\lambda_{2} = \frac{\exp(-\Delta_{d}/kT) - \exp(-\Delta_{s}/kT)}{1 + 2\exp(-\Delta_{d}/kT) + \exp(-\Delta_{s}/kT)};$$
(4)

the upper and lower signs pertain respectively to the positions of the fluorine atoms F_1 and F_2 , $\Delta_d = 27 \text{ cm}^{-1}$,^[2] $\Delta_s = 56 \text{ cm}^{-1}$.^[3].

In computing the local fields from the higher-order multipole moments, we used the values $\langle r^2 \rangle = 0.62$ a.u., $\langle r^4 \rangle = 0.95$ a.u., and $\langle r^6 \rangle = 3.13$ a.u., which were obtained with the Hartree-Fock wave functions of the Tm³⁺ ion.^[7] As was to be expected from general considerations, the calculation yielded for the nondipole contribution to the direct local field a value much smaller than (3), to wit,

$$10^{3} H_{loc}^{nondip} H_{0} = 0.37 \lambda_{1} + 0.60 \lambda_{2} \pm (0.14 \lambda_{1} + 0.25 \lambda_{2}) \cos 2\varphi$$
(5)
 $\mp (0.13 \lambda_{1} + 0.22 \lambda_{2}) \sin 2\varphi.$

It can be seen from the formula (5) that the local-field component arising upon the occupation of the doublet $|d\rangle$ and the field due to the multipole moments of the ground state of the Tm^{3*} ion have the same direction, and, consequently, as the temperature is raised, the local field should decrease more slowly than the paramagnetic susceptibility of the crystal. In the presence of not only a quantitative, but also a qualitative disagreement of the theory with experiment, it remains to acknowledge that the direct contribution cannot bear the responsibility for the anomalous temperature dependence of the local magnetic field.

Let us now consider the contribution made by the Pauli forces to the local magnetic field. In trying to take directly into account the indistinguishability of the electrons of the rare-earth ion and the ligands in the region where their orbits overlap (as is done, for example, in the method of molecular orbitals), we find it is no longer possible to speak of multipole moments of thulium, since the Tm^{3*} and F^{-} ions cannot be considered to be statistically independent subsystems. We shall get over this difficulty and be able to use in the calculations single-ion wave functions if we replace the antisymmetric—with respect to permutations of all the electrons (including interchange of electrons between thulium and fluorine)—wave functions by the product of the functions of the individual ions and transform the Hamiltonian (2) into an effective operator \mathcal{H}_{eff} according to the rule^[8]

$$\mathcal{H}_{eff} = \mathcal{H} + \mathcal{H}_{ex} = \mathcal{H} - \frac{\mathcal{H}P + P\mathcal{H}}{2} + \frac{1}{2} \sum_{\alpha} \mathcal{H} |\alpha\rangle \langle \alpha| P + \frac{1}{2} \sum_{\alpha} P |\alpha\rangle \langle \alpha| \mathcal{H};$$
(6)

as a result of such transformations the mean values of the physical quantities remain unchanged up to the second powers of the thulium-fluorine overlap integrals. In the effective Hamiltonian (6) the symbol P denotes the operator of paired inter-ionic electron transpositions, \mathcal{X} is the electron-nucleus interaction Hamiltonian (2), the index α numbers the various products of the thulium and fluorine wave functions and assumes values corresponding to only the ground-state $4f^{A2}$ electronic configuration of the thulium ion.

The first operator in (6), which corresponds in the basis of the products of the wave functions of the individual ions to the interaction of the nuclear moment of fluorine with the direct local field, has already been discussed above. Let us consider the next operators in \mathcal{H}_{off} connected with the inter-ionic transpositions of the electrons. Going over in (6) to the moment representation, and performing the necessary unitary transformations, we find it convenient to represent the exchange-interaction Hamiltonian in the form

$$\mathscr{H}_{ex} = \beta \gamma \hbar [a_{1}JI + a_{2}[-JI + 3R^{-2}(IR) (JR)] + a_{3}(\{V^{(5)}C^{(1)}\}^{(1)}I^{(1)}) + a_{4}(\{V^{(5)}C^{(4)}\}^{(1)}I^{(1)}) + a_{5}(\{V^{(5)}C^{(1)}\}^{(1)}I^{(1)} + a_{6}(\{V^{(5)}C^{(6)}\}^{(1)}I^{(1)}) + a_{7}(\{V^{(7)}C^{(6)}\}^{(1)}I^{(1)}) + a_{8}(\{V^{(7)}C^{(6)}\}^{(1)}I^{(1)})].$$

$$(7)$$

Here the operators of the higher multipole moments of thulium have been written in terms of the irreducible tensor operators $V^{(k)}$, $C^{(k)}$, spherical tensors that fix the direction of the radius vector of the selected $\text{Tm}^{3^{+}} - \mathbf{F}^{-}$ pair, the curly and round brackets in the expressions $(\{VC\}I\}$ denote respectively the direct and scalar products of the tensors. The quantities a_i are linear combinations of the two-center integrals, which were computed with the Hartree-Fock functions of the $\text{Tm}^{3^{+}[7]}$ and $\mathbf{F}^{-[3]}$ ions. It turned out that the exchange local field at a fluorine nucleus is determined only by the two nearest thulium ions, located at distances R_1 and R_2 , which are such that $a_i(R_1)/a_i(R_2) = 1.36$ for all a_i and $S_1(R_2)/S_0(R_2) = -0.63$.

Combining (7) with the Zeeman interaction Hamiltonian $g\beta H \cdot J$ in second-order perturbation theory, we find the exchange local field

$$H_{1oc}^{ex}/H_{0} = [3.74\lambda_{1} + 6.80\lambda_{2} \pm (0.24\lambda_{1} - 2.67\lambda_{2})\cos 2\varphi] \\ \pm (16.40\lambda_{1} - 16.20\lambda_{2})\sin 2\varphi]f_{s}(R_{2})$$

$$+ [-1.11\lambda_{1} - 1.18\lambda_{2} \mp (0.11\lambda_{1} + 0.08\lambda_{2})\cos 2\varphi \mp (0.16\lambda_{1} + 0.21\lambda_{2})\sin 2\varphi]S_{0}^{2}(R_{2})$$

~...

in the form of a sum of contributions corresponding to the overlap of the 4f orbits of thulium with the 1s, 2s (the parameter f_s), and 2p (the parameter S_0^2) orbits of fluorine. It is interesting to note that the greatest contribution to the contact part of (8) is made by the highest multipole moment (the last operator in (7)). According to the numerical calculation, $S_0^2(R_2) = 6 \times 10^{-4}$ a.u., and the contribution to the local field due to the overlap of the 4f orbits with the 2p orbits is practically canceled out by the direct nondipole contribution (5). Then from (8) we obtain for the computation of the angular and temperature dependences of the local fields a formula containing only one parameter, f_s , characterizing the magnitude of the exchange contact interaction. It is easy to see that this formula qualitatively explains the experimentally observed anomalous temperature dependence $H_{loc}(T)$: the local-field component arising upon the occupation of the $|d\rangle$ doublet and the low-temperature component are oppositely directed, and, consequently, as the temperature is raised, the resultant local field decreases more rapidly than the magnetization of the sample.

In order to carry out a quantitative comparison, we summed up the point-dipole field (3) and the exchange field (8), and assigned the value $f_S(R_2) = 4.3 \times 10^{-3}$ a.u. on the basis of the maximum width of the $H_{1oc}(F_1)$ $-H_{1oc}(F_2)$ spectrum at liquid-helium temperatures. Notice that the assumed f_S value is not at variance with the data on the electron-nuclear double resonance in fluorite crystals containing Kramers rare-earth ions.^[51] The final formula for the computation of the local fields produced at the fluorine nuclei by the thulium ions assumes the form

$$\frac{10^{3}H_{100}/H_{0} = 18.5\lambda_{1} + 32.1\lambda_{2} \pm [(4.3\lambda_{1} - 7.61\lambda_{2})^{2} + (54.4\lambda_{1} - 74.3\lambda_{2})^{3}]^{\frac{1}{7}} \sin 2\varphi; \qquad (9)$$

in this formula the zero of the angle φ corresponds to the equality, $H_{loc}(\mathbf{F}_1) = H_{loc}(\mathbf{F}_2)$, of the local fields. The continuous curves in Figs. 2 and 4 are theoretical curves computed from the formula (9); it can be seen that the theory agrees satisfactorily with experiment. Thus, at liquid-helium temperatures the exchange field accounts for more than 85% of the quantity H_{loc} .

The dominating role of the exchange interaction in the thulium-fluorine system is also indicated by the fine structure of the NMR lines of ¹⁹F (Fig. 5). The measurements showed that the intervals between the finestructure components are maximal when the width of the NMR spectrum of fluorine has its maximum value, and they are then 10-20 Oe. As the temperature is raised, the intervals decrease and the fine structure gets concealed in the line width. The dipole-dipole interaction of the nuclear moments of ¹⁹F with each other and with the nuclear moments of ¹⁶⁹Tm explains neither the absolute value of the fine splittings, nor the temperature dependence of these splittings. The fine structure should be regarded as the manifestation of the interaction of a small number of particles forming an isolated group. In the LiTmF₄ crystal lattice such groups can be produced only by short-range (exchange) forces. As has been shown above, the fluorine nucleus is strongly coupled via the exchange field of the multipoles to the electron shells of the two Tm³⁺ ions closest to it (on account of the fact that $f_s(R) \sim \exp(-4.5R)$, the interaction with the other thulium ions is at least 100 times weaker). In their turn the electron shells of the thulium ions are coupled to the intrinsic nuclear moments of ¹⁶⁹Tm $(I=\frac{1}{2})$



FIG. 5. NMR spectrum of ¹⁹F in the LiTmF₄ crystal; T = 4.2 K, $\nu = 10,600$ kHz, $H \perp c$, $\varphi = 30^{\circ}$.

by the hyperfine interaction

$$\mathscr{H}_{\rm hf} = a {\rm JI}, \tag{10}$$

where a = -393.5 MHz (Ref. 1, Vol. 1, p. 335). Thus, there arises an indirect interaction between the nuclear moment of a fluorine atom and two nuclear moments of thulium.¹⁾

Combining (7) and (10) in second-order perturbation theory, we find the Hamiltonian of this interaction

$$\mathcal{H}_{B} = \sum_{A=\mathrm{Tm}_{1},\mathrm{Tm}_{2}} \{ C_{1}^{AB} (I_{+}^{A}I_{-}^{B} + I_{-}^{A}I_{+}^{B}) + i C_{2}^{AB} (I_{+}^{A}I_{-}^{B} - I_{-}^{A}I_{+}^{B}) \\ + C_{3}^{AB} (I_{+}^{A}I_{+}^{B} + I_{-}^{A}I_{-}^{B}) + i C_{4}^{AB} (I_{+}^{A}I_{+}^{B} - I_{-}^{A}I_{-}^{B}) \}.$$
(11)

For the f_s , S_0 , and S_1 values chosen above, the calculation leads to the following expressions for the parameters C_i^{AB} (in kHz):

$$C_{1}(\operatorname{Tm}_{1}F_{1}) = C_{1}(\operatorname{Tm}_{2}F_{2}) = 20\lambda_{1} - 9\lambda_{2},$$

$$C_{2}(\operatorname{Tm}_{1}F_{1}) = C_{2}(\operatorname{Tm}_{2}F_{2}) = 1.3\lambda_{1} + 0.7\lambda_{2},$$

$$C_{3}(\operatorname{Tm}_{1}F_{1}) = -C_{3}(\operatorname{Tm}_{2}F_{2}) = -8.1\lambda_{1} + 1.7\lambda_{2},$$

$$C_{4}(\operatorname{Tm}_{4}F_{1}) = -C_{4}(\operatorname{Tm}_{2}F_{2}) = -19.5\lambda_{1} - 13\lambda_{2},$$

$$C_{1}(\operatorname{Tm}_{2}F_{1}) = C_{1}(\operatorname{Tm}_{1}F_{2}) = -12.1\lambda_{1} + 23.2\lambda_{2},$$

$$C_{2}(\operatorname{Tm}_{2}F_{1}) = -C_{3}(\operatorname{Tm}_{1}F_{2}) = -16.5\lambda_{1} + 18.5\lambda_{2},$$

$$C_{3}(\operatorname{Tm}_{2}F_{1}) = -C_{3}(\operatorname{Tm}_{1}F_{2}) = -8.6\lambda_{1} + 7.3\lambda_{2},$$

$$C_{4}(\operatorname{Tm}_{2}F_{1}) = -C_{4}(\operatorname{Tm}_{1}F_{2}) = -14.6\lambda_{4} + 20\lambda_{2},$$
(12)

Numerical estimates of the interaction energy of the magnetic moments of the nuclei in the LiTmF₄ crystal at the liquid-helium temperature give: 0.4 kHz or 0.1 Oe for the ¹⁹F-¹⁶⁹Tm dipole-dipole interaction, 1.5 kHz or 0.4 Oe for the ¹⁹F-¹⁹F dipole-dipole interaction, and 40 kHz or 10 Oe for the indirect ¹⁹F-¹⁶⁹Tm interaction. Thus, the numerical computation finally convinces us that it is precisely the indirect ¹⁹F-¹⁶⁹Tm interaction that is responsible for the appearance of the fine structure in the NMR spectrum of ¹⁹F. The decrease of the fine splittings with increasing temperature is explained by changes in the interaction parameters C_i^{AB} , (12).

In conclusion, it should be emphasized that underlying the success of the above-performed analysis is the use of new operator forms in the electron-nucleus interaction Hamiltonian. It has been experimentally demonstrated that, owing to the Pauli exchange forces, the higher magnetic multipole moments can make a significant contribution to the energy of interaction of the paramagnetic ion with the ligands. A short-range anisotropic interaction between the nuclear magnetic moments of the rare-earth ion and the ligand has been identified for the first time. The significance of the obtained results goes beyond the limits of the present paper; the magnetic multipole moments can manifest themselves in the interaction of any rare-earth ion with the ligands and the external fields, and can, consequently, be observed by the methods of the electron-nuclear double resonance and optical and γ -ray spectroscopies.

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Spin waves in a medium with nonequilibrium spin orientation

A. G. Aronov

B. P. Konstantinov Nuclear Physics Institute, USSR Academy of Sciences, Leningrad (Submitted November 29, 1976) Zh. Eksp. Teor. Fiz. 73, 577-582 (August 1977)

The small exchange interaction which exists in any material leads, in the presence of nonequilibrium polarization of the electrons, to the appearance of spin waves with a quadratic dispersion law at small momenta. The spin waves exist for either sign of the exchange interaction and for any degree of degeneracy of the electron gas. The Landau damping of these waves is small compared with their frequency.

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In the discussions of the phenomena that arise during spin injection^[1] and optical orientation of spins^[2] in semiconductors and metals the exchange interaction has been disregarded on the grounds that it is small. In this article we shall show that allowance for the small exchange interaction leads to a qualitatively new phenomenon—the existence of spin waves in a medium with spins oriented in a nonequilibrium manner. Moreover, we shall show that these waves exist for either sign of the exchange interaction and for any degree of degeneracy, and that their damping is small compared with their frequency.

The simplest way to obtain the dispersion law of the spin waves is to calculate the spin part of the magnetic susceptibility, just as is done, e.g., in the Stoner model of ferromagnets (cf., e.g., ^[31]), and investigate its poles. In the self-consistent field model the exchange interaction between the electrons leads to the result that the energy of particles with a given spin depends on their distribution function.

For simple parabolic bands,

$$\varepsilon_{\alpha}(\mathbf{k}) = k^2/2m - \sum_{\mathbf{k}'} V_{\mathbf{k}-\mathbf{k}'} n_{\alpha}(\mathbf{k}').$$
(1)

Here, $V_{\mathbf{k}-\mathbf{k}'}$ is a Fourier component of the potential of the exchange interaction. In Landau's Fermi-liquid theory, $V_{\mathbf{k}-\mathbf{k}'}$ is related to the antisymmetric scattering amplitude. For a nondegenerate electron gas the simplest approximation for the potential $V_{\mathbf{k}-\mathbf{k}'}$ is a screened Coulomb potential. However, despite the fact that it is possible to establish the dispersion law at small momenta for any form of the potential, it has not been possible to calculate the constants, even for the screened Coulomb potential. Therefore, in the following we take it that

$$\varepsilon_{\alpha}(\mathbf{k}) = \frac{k^2}{2m} - \frac{I}{N} \sum_{\mathbf{k}'} n_{\alpha}(\mathbf{k}').$$
(2)

We observe immediately that the constant $I \sim Ne^2/mT \ll T$ for a nondegenerate gas and $I \sim e^2 N^{1/3} < \mu$ in the case of degeneracy.

Calculating the response to an external magnetic field

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¹⁾The possibility of an indirect interaction of the nuclear moments via the exchange-coupled electron shells was pointed out in the work of one of the present authors.^[10]