

THE EFFECT OF THE MULTIPLICITY OF *d* (*f*) SHELLS ON ELECTRON INTERACTION IN CRYSTALS

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The exchange model is generalized by taking into account variation of multiplicity of the *d* or *f* shells induced by conduction electrons. The Hamiltonian for direct exchange interaction of *d* electrons is generalized and the properties of the corresponding multiplicity excitation waves are discussed. The effect of changes of multiplicity on appearance of superconductivity and also on the ordering of the conduction electron spins and *d* shell spins is considered within the framework of the generalized *s-d* exchange model.

1. In treating the exchange interaction of conduction electrons with unfilled *d* (or *f*) shells¹⁾ (the *s-d* exchange model^[1]), one is usually restricted to a Hamiltonian of the form^[2,3]

$$H_1 = -N^{-1} \sum_{\mathbf{k}, \mathbf{k}', n} I(\mathbf{k} - \mathbf{k}') \exp [i(\mathbf{k} - \mathbf{k}') \mathbf{R}_n] \{ (a_{\mathbf{k}'\uparrow}^* a_{\mathbf{k}\uparrow} - a_{\mathbf{k}'\downarrow}^* a_{\mathbf{k}\downarrow}) S_n^z + a_{\mathbf{k}'\uparrow}^* a_{\mathbf{k}\downarrow} S_n^- + a_{\mathbf{k}'\downarrow}^* a_{\mathbf{k}\uparrow} S_n^+ \}, \quad (1)$$

where *N* is the number of crystal lattice sites, *I*(**k** - **k'**) is the Fourier component of the *s-d* exchange integral, **k** and **k'** are the wave vectors of the conduction electron, **R_n** and **S_n** are the radius vector and spin operator of the *n*-th transition ion, **S_n[±]** = **S_n^x** ± *iS_n^y*, and *a_{kσ}^{*}* and *a_{kσ}* are the Fermi creation and annihilation operators of a conduction electron in a state with wave vector **k** and spin projection *σ*. The Hamiltonian (1) can be written in the form^[1,2]

$$H_1 = - \sum_{i, n} I(\mathbf{R}_n - \mathbf{r}_i) S_n \sigma_i, \quad (2)$$

where **r_i** is the radius vector of the *i*-th conduction electron, and *I*(**R_n** - **r_i**) is the exchange integral between the *n*-th ion and the *i*-th electron.

Equations (1) and (2) do not completely describe the *s-d* interaction. Since the operators **S_n^{Z, ±}** commute with the operator **S_n²**, this Hamiltonian describes processes with conservation not only of the total spin of the whole system, but also of the spins of every *d*-shell. Consequently, (1) and (2) take into account the possibility of a change in the spin projection of the *d*-shell, but not in its multiplicity as a result of its exchange interaction with the

¹⁾For simplicity we shall write only the symbol for the *d* shell, with the understanding that we are dealing with both the *d* and the *f* shells of transition and rare-earth ions.

conduction electrons. Moreover, the calculation of exchange processes associated with a variation of the magnitude of the spin of the *d* shell can be important for a number of phenomena (superconductivity, spin ordering, electrical resistance, etc.). Therefore, it is expedient to add to the Hamiltonian (1) terms that describe processes involving a change in multiplicity of the *d* states.

2. To solve this problem one can start with the *s-d* exchange Hamiltonian described in Fermi operators of second quantization. For simplicity we shall first consider the case of two *d* electrons on each transition ion in different states: *ψ_α* and *ψ_β*. Then the desired Hamiltonian takes the form

$$H' = -N^{-1} \sum_{\lambda, \mathbf{k}, \mathbf{k}', n} I_{\lambda, \mathbf{k}, \mathbf{k}', n} a_{n\lambda\sigma_1}^* a_{n\lambda\sigma_2} a_{\mathbf{k}'\sigma_2}^* a_{\mathbf{k}\sigma_1}, \quad (3)$$

where *λ* = *α, β*; *a_{nλσ}^{*}* and *a_{nλσ}* are the Fermi creation and annihilation operators respectively of a *d* electron on the *n*-th site in state *ψ_{λσ}*;

$$I_{\lambda, \mathbf{k}, \mathbf{k}', n} = \exp [i(\mathbf{k} - \mathbf{k}') \mathbf{R}_n] I_{\lambda}(\mathbf{k} - \mathbf{k}'); \quad (4)$$

the summation in (3) is over **k**, **k'**, *n*, *σ₁*, *σ₂*, *λ*. Converting from second quantization operators to spin operators, we transform (3) to the form

$$H' = H_1 + \tilde{H}_1 - N^{-1} \sum_{\mathbf{k}, \mathbf{k}', n} \frac{1}{2} (I_{\alpha, \mathbf{k}, \mathbf{k}', n} + I_{\beta, \mathbf{k}, \mathbf{k}', n}) \times (a_{\mathbf{k}'\uparrow}^* a_{\mathbf{k}\uparrow} + a_{\mathbf{k}'\downarrow}^* a_{\mathbf{k}\downarrow}), \quad (5)$$

where *H₁* is the Hamiltonian (1) with *I* = 1/2 (*I_α* + *I_β*) and **S_n** = **S_{nα}** + **S_{nβ}**, and

$$\tilde{H}_1 = -N^{-1} \sum_{\mathbf{k}, \mathbf{k}', n} \frac{1}{2} (I_{\alpha, \mathbf{k}, \mathbf{k}', n} - I_{\beta, \mathbf{k}, \mathbf{k}', n}) \{ (a_{\mathbf{k}'\uparrow}^* a_{\mathbf{k}\uparrow} - a_{\mathbf{k}'\downarrow}^* a_{\mathbf{k}\downarrow}) A_n^z + a_{\mathbf{k}'\uparrow}^* a_{\mathbf{k}\downarrow} A_n^- + a_{\mathbf{k}'\downarrow}^* a_{\mathbf{k}\uparrow} A_n^+ \}, \quad (6)$$

$$A_n^{z, \pm} = S_{n\alpha}^{z, \pm} - S_{n\beta}^{z, \pm}. \quad (7)$$

The table shows the effect of the operators on the wave functions of the singlet state Ψ_0^S and of the triplet states Ψ_0^T , Ψ_1^T , Ψ_{-1}^T with spin projections 0, +1, -1:

	A^z	A^-	A^+	$(A^-)^2$	$(A^+)^2$	$(A^-)^3$	$(A^+)^3$
Ψ_0^S	Ψ_0^T	$\sqrt{2}\Psi_{-1}^T$	$-\sqrt{2}\Psi_1^T$	0	0	0	0
Ψ_0^T	Ψ_0^S	0	0	0	0	0	0
Ψ_1^T	0	$-\sqrt{2}\Psi_0^S$	0	$-2\Psi_{-1}^T$	0	0	0
Ψ_{-1}^T	0	0	$\sqrt{2}\Psi_0^S$	0	$-2\Psi_1^T$	0	0

It is clear that unlike the operators $S_n^{z, \pm}$, which act only on the spin projection, the operators $A_n^{z, \pm}$ also change the spin magnitude, i.e., the multiplicity of the wave function. The quantity \tilde{H}_1 therefore represents the usually neglected part of the exchange Hamiltonian that describes processes of singlet-triplet transitions of unfilled d and f shells.

The Hamiltonian \tilde{H}_1 of (6) differs from the H_1 of (1) by the replacement of the sums of exchange integrals and spin operators of the states α and β by their corresponding differences. It is easily shown that \tilde{H}_1 can also be written in a more compact form:

$$\tilde{H}_1 = - \sum_{i, n} \tilde{I}(\mathbf{R}_n - \mathbf{r}_i) \mathbf{A}_n \sigma_i,$$

$$\tilde{I}(\mathbf{R}_n - \mathbf{r}_i) = 1/2 [I_\alpha(\mathbf{R}_n - \mathbf{r}_i) - I_\beta(\mathbf{R}_n - \mathbf{r}_i)]. \quad (8)$$

Although the Hamiltonian \tilde{H}_1 also contains operators that change the magnitude of the spin of individual d shells, as a whole it, like H_1 , conserves the total spin of the entire system of conduction electrons and d shells.

Combining (8) and (2), with the following substitution in (2),

$$I(\mathbf{R}_n - \mathbf{r}_i) = 1/2 [I_\alpha(\mathbf{R}_n - \mathbf{r}_i) + I_\beta(\mathbf{R}_n - \mathbf{r}_i)],$$

$$\mathbf{S}_n = \mathbf{S}_{n\alpha} + \mathbf{S}_{n\beta},$$

we obtain

$$H_{\text{ex}} = H_1 + \tilde{H}_1 = - \sum_{i, n, \lambda} I_\lambda(\mathbf{R}_n - \mathbf{r}_i) \mathbf{S}_{n\lambda} \sigma_i. \quad (9)$$

Equation (9) corresponds to the Dirac relation^[4] for the interaction energy of electrons with spins 1/2 to first order in perturbation theory. Hence we can say that the inclusion in the s-d exchange Hamiltonian (9) of terms describing processes of multiplicity change amounts to a calculation of the interaction of the conduction electrons not only with the resultant spin \mathbf{S}_n of the d electrons of the n-th ion, but also with the spin $\mathbf{S}_{n\lambda}$ of each of its states λ separately. This permits the generalization of the above result to the case $2 < \nu \leq 2(2l + 1)$ of

electrons in an unfilled shell corresponding to orbital quantum number l . That is, setting $\lambda = 1, 2, \dots, \nu$ in (9) and using the identity

$$\sum_{\lambda=1}^{\nu} I_\lambda(\mathbf{R}_n - \mathbf{r}_i) \mathbf{S}_{n\lambda} = \frac{1}{\nu} \sum_{\lambda=1}^{\nu} I_\lambda(\mathbf{R}_n - \mathbf{r}_i) \mathbf{S}_n$$

$$+ \frac{1}{\nu} \sum_{\lambda_1 < \lambda_2} [I_{\lambda_1}(\mathbf{R}_n - \mathbf{r}_i) - I_{\lambda_2}(\mathbf{R}_n - \mathbf{r}_i)] \mathbf{A}_{n, \lambda_1, \lambda_2}, \quad (10)$$

where

$$\mathbf{S}_n = \sum_{\lambda=1}^{\nu} \mathbf{S}_{n\lambda}, \quad \mathbf{A}_{n, \lambda_1, \lambda_2} = \mathbf{S}_{n\lambda_1} - \mathbf{S}_{n\lambda_2},$$

we obtain

$$H_1 = - \sum_{i, n} \frac{1}{\nu} \sum_{\lambda=1}^{\nu} I_\lambda(\mathbf{R}_n - \mathbf{r}_i) \mathbf{S}_n \sigma_i,$$

$$\tilde{H}_1 = - \sum_{i, n} \frac{1}{\nu} \sum_{\lambda_1 < \lambda_2} [I_{\lambda_1}(\mathbf{R}_n - \mathbf{r}_i) - I_{\lambda_2}(\mathbf{R}_n - \mathbf{r}_i)] \mathbf{A}_{n, \lambda_1, \lambda_2} \sigma_i, \quad (11)$$

where H_1 coincides with the usual Hamiltonian (2) (for which, of course, it is necessary to set $I = (1/\nu) \sum I_\lambda$) and \tilde{H}_1 is the part of the Hamiltonian that takes into account transitions with a change in multiplicity of the ions of the transition elements.

In this way terms can be added to the Hamiltonian of the s-d exchange model that describe a change in multiplicity of the d shells, taking into account along with the exchange integrals \tilde{I} and spin operators that are symmetric with respect to the orbital states the antisymmetric ones as well.²⁾ This is of great significance. In fact, in the usual treatment of the exchange of conduction electrons and d-shell spins, as well as indirect or direct exchange, the Dirac equation^[4], which was derived for the case $S_n = 1/2$, is applied to the case $S_n > 1/2$. Such a generalization is not rigorous, since it leaves out the possibility of a change in the magnitude of the spin of the n-th ion S_n (to which corresponds the assumption of absolute invariance of this quantity), as well as a number of possible values of the resultant spin of different ions. It is clear that the Hamiltonian (11), which is based on

²⁾The proposed generalization of the s-d model can therefore be formulated in the framework of the semi-phenomenological treatment with a Hamiltonian

$$H = a_1 \sigma \mathbf{S} + a_2 \sigma \mathbf{A},$$

where the exchange energy parameter a_1 and the spin operator \mathbf{S} are both symmetric with respect to the orbital states and the parameter a_2 and the operator \mathbf{A} are both antisymmetric. However, for concrete applications using microscopic representations it is more logical to start from the s-d exchange Hamiltonian model.

the identity (10), which pertains to spins $S_{n\lambda} = 1/2$, is free of these insufficiencies. It permits making the idea of "rigidity" of the d-shell spin more precise. It is obvious that with respect to s-d exchange the degree of rigidity of S_n is governed not so much by the Hund energy, as is customarily thought, as by the smallness of the difference of the exchange integrals I_{λ_1} and I_{λ_2} , since for $I_{\lambda_1} \approx I_{\lambda_2}$, the principal rôle is played by H_1 , which involves the resultant spin of the ion

$$S_n = \sum_{\lambda=1}^{\nu} S_{n\lambda}.$$

3. While we had in mind above the possibility of applying the theory to the case of an impurity of transition element ions in other metals, we had not assumed a periodic arrangement of these ions in the crystal lattice. If, however, they are arranged periodically, then the excitation of the multiplicity of one ion does not remain, generally speaking, localized on it—as a consequence of the exchange interaction with its neighbors, the excitation will propagate through the crystal. The treatment of the exchange interaction of triplet and singlet d shells (which represent the simplest possibility for the propagation of multiplicity waves) is conveniently carried through by using the operators B defined by Eq. (A-1) of the Appendix.

Namely, if we start from the Hamiltonian of a system of d electrons written in the form of second quantization^[5] and limit ourselves to integrals that contain no more than two overlapping wave functions $\psi_{n_1\lambda_1}$ and $\psi_{n_2\lambda_2}$ (where $n_1 \neq n_2$), then it is easy to obtain, using Eq. (A-2) of the Appendix, the following expression:

$$\begin{aligned} H = & 2 \left(NE_0 + \sum_n K_n + \sum_{n \neq m} K_{nm} \right) \\ & + \sum_n K_{nn} - \sum_n I_{n\alpha; n\beta} (1 - 2P_n) \\ & - \sum_{n \neq m} J_{nm} [1 + (Q_n - L_n)(Q_m - L_m) \\ & + (B_n^*{}^T B_{n\downarrow} + B_{n\uparrow}^*{}^T B_n^T) (B_{m\downarrow}^*{}^T B_m^T + B_m^*{}^T B_{m\uparrow}) + \text{c.c.}] \\ & - \sum_{n \neq m} J'_{nm} [(B_n^*{}^S B_n^T + B_n^*{}^T B_n^S) \\ & \times (B_m^*{}^S B_m^T + B_m^*{}^T B_m^S) + (B_n^*{}^S B_{n\downarrow} - B_{n\uparrow}^*{}^S B_n^S) \\ & \times (B_{m\downarrow}^*{}^S B_m^S - B_m^*{}^S B_{m\uparrow}) + \text{c.c.}] \\ & - \sum_{n \neq m} J''_{nm} [(B_n^*{}^S B_n^T + B_n^*{}^T B_n^S)(Q_m - L_m) \\ & + (B_n^*{}^S B_{n\downarrow} - B_{n\uparrow}^*{}^S B_n^S) (B_{m\downarrow}^*{}^T B_m^T + B_m^*{}^T B_{m\uparrow}) + \text{c.c.}] \end{aligned}$$

$$\begin{aligned} & - \sum_{n \neq m} J''_{nm} [(Q_n - L_n) (B_m^*{}^S B_m^T + B_m^*{}^T B_m^S) \\ & + (B_n^*{}^T B_{n\downarrow} + B_{n\uparrow}^*{}^T B_n^T) (B_{m\downarrow}^*{}^S B_m^S - B_m^*{}^S B_{m\uparrow}) + \text{c.c.}], \end{aligned} \quad (12)$$

where N is the number of transition ions; E_0 is the energy of the d level of an isolated atom; K_n is the integral of Coulomb attraction of the d electron of the n-th ion by the positive (without accounting for their d electrons) kernels of the other ions; K_{nm} and $I_{n\alpha; m\beta}$ are the Coulomb repulsion integral and exchange integral, respectively, of the d electron of the n-th ion with the d electron of the m-th ion; K_{nn} and $I_{n\alpha; n\beta}$ are the Coulomb repulsion and exchange integral, respectively, of two d electrons of the same n-th ion; the numbers P_n , Q_n , and L_n are equal to unity, if the ion is respectively a singlet, a right triplet, or a left triplet, and, on the other hand, equal to zero in all remaining cases. The exchange integrals J_{nm} are defined by the expressions

$$\begin{aligned} J_{nm} &= 1/4 (I_{n\alpha; m\alpha} + I_{n\alpha; m\beta} + I_{n\beta; m\alpha} + I_{n\beta; m\beta}), \\ J'_{nm} &= 1/4 (I_{n\alpha; m\alpha} - I_{n\alpha; m\beta} - I_{n\beta; m\alpha} + I_{n\beta; m\beta}), \\ J''_{nm} &= 1/4 (I_{n\alpha; m\alpha} + I_{n\alpha; m\beta} - I_{n\beta; m\alpha} - I_{n\beta; m\beta}), \\ J'''_{nm} &= 1/4 (I_{n\alpha; m\alpha} - I_{n\alpha; m\beta} + I_{n\beta; m\alpha} - I_{n\beta; m\beta}). \end{aligned} \quad (13)$$

The term $-I_{n\alpha; n\beta} (1 - 2P_n)$ in (12) describes the intra-atomic exchange energy of excitation of a singlet state, if in accordance with Hund's rule it is assumed that $I_{n\alpha; n\beta} > 0$. Then the energy of the singlet state of the d shell exceeds by $2I_{n\alpha; n\beta}$ the magnitude of the energy of each of the three possible triplet states, which in (12) are degenerate for an isolated shell (i.e., without considering the exchange interaction of the different shells). For simplicity we shall assume that this degeneracy is lifted (as a result of the interaction of the different shells among themselves or with the conduction electrons) and that respectively in the ground state all shells are described either by the functions Ψ_0^T , generated by the operators $B_n^*{}^T$, or by the functions Ψ_1^T , generated by the operators $B_{n\uparrow}^*{}^T$.³⁾ In the first case, limiting the treatment to the ground triplet state Ψ_0^T (with zero spin projection) and excited singlet states Ψ_0^S (generated by operators $B_n^*{}^S$) greatly simplifies the Hamiltonian (12), which takes the form

³⁾ Obviously the ferromagnetic ground state is also obtained by assuming that all d shells are described by the functions Ψ_{-1}^T .

$$H = \text{const} + 2\nu_0 I_{n\alpha; n\beta}$$

$$- \sum_{n \neq m} J_{nm} (B_n^* T B_n^S B_m^* S B_m^T + B_n^* S B_n^T B_m^* T B_m^S), \quad (14)$$

where ν_0 is a fixed number of excited singlet states.

In the Hamiltonian (14) it is convenient to go over to operators of creation b_n^* and annihilation b_n at the n -th site of singlet excitation or para-excitation:

$$b_n^* = B_n^* S B_n^T, \quad b_n = B_n^* T B_n^S. \quad (15)$$

By means of a Fourier transformation (14) can be written in the form

$$H = \text{const} + \sum_{\mathbf{k}} E_{\mathbf{k}}^S n_{\mathbf{k}}^S, \quad (16)$$

where $n_{\mathbf{k}}^S$ is the number of parawaves with energy

$$E_{\mathbf{k}}^S = 2I_{n\alpha; n\beta} - 2 \sum_{\mathbf{h}} \tilde{J}(\mathbf{h}) \cos \mathbf{k} \mathbf{h} \quad (17)$$

(\mathbf{h} is the distance between the n -th and m -th sites). It is clear from (17) that for small wave vectors \mathbf{k} the parawaves propagated in an ortho medium have, like ferromagnetic spin waves, a quadratic dispersion law. Clearly, however, the parawaves are essentially different from the spin waves, since they can propagate even in the absence of ferromagnetic ordering in the ground state.

The parawaves can, of course, propagate also in a ferromagnetic medium. Assuming, for example, that all d shells are described in the ground state by functions Ψ_1^T , discarding the para- and ortho-excitation interaction terms, and also considering as fixed the total number of ortho- and para-excitations, we obtain from (12):

$$H = \text{const} + \sum_{\mathbf{k}} E_{\mathbf{k}}^T n_{\mathbf{k}}^T + \sum_{\mathbf{k}} E_{\mathbf{k}}^S n_{\mathbf{k}}^S, \quad (18)$$

where

$$E_{\mathbf{k}}^T = 2 \sum_{\mathbf{h}} J(\mathbf{h}) [1 - \cos \mathbf{k} \mathbf{h}]. \quad (19)$$

We note that the translational energy of a parawave

$$-2 \sum_{\mathbf{h}} \tilde{J}(\mathbf{h}) \cos \mathbf{k} \mathbf{h}$$

can give a negative contribution to the parawave energy (e.g., when $\tilde{J}(\mathbf{h}) > 0$ for $\mathbf{k} = 0$, and when $\tilde{J}(\mathbf{h}) < 0$ in proximity to a neighbor for $\mathbf{k}_x = \mathbf{k}_y = \mathbf{k}_z = \pi/a$, where a is the crystalline lattice constant). Thus, interatomic translational exchange can decrease the energy of excitation of the parastate compared to the magnitude of the intra-atomic exchange energy $2I_{n\alpha; n\beta}$ characteristic of an isolated⁴⁾ shell. This does not allow neglecting the

⁴⁾This result is analogous to the possibility established in the polar model of a crystal [6] of lowering the excitation energy of "pairs" on account of a transfer integral.

parawaves compared to the orthowaves,⁵⁾ although excitation of a parawave may require that a certain "threshold" energy be overcome.

Using the operators A_n and S_n , we can write (12) in the form

$$H = 2 \left(NE_0 + \sum_n K_n + \sum_{n \neq m} K_{nm} \right) + \sum_n K_{nn} - \sum_n I_{n\alpha; n\beta} (1 - 2P_n) - \sum_{n \neq m} \{ J_{nm} [1 + S_n S_m] + J_{nm}' A_n A_m + J_{nm}'' A_n S_m + J_{nm}''' S_n A_m \}. \quad (20)$$

From (20) it is seen that when there is more than one d electron the usual exchange Hamiltonian, which contains only products of the type $S_n S_m$, does not describe the exchange completely. The additional terms of type $A_n A_m$ and $A_n S_m$ describe processes in which the magnitude of the spin of the d shells changes (and not only its projection) and, consequently, in which their multiplicity changes.

Using (13), it is not difficult to prove that the part of (20) that describes the exchange interaction between different n -th and m -th ions has the form

$$H_{\text{ex}} = - \sum_{n \neq m} \sum_{\lambda_1, \lambda_2} I_{n\lambda_1; m\lambda_2} S_{n\lambda_1} S_{m\lambda_2}. \quad (21)$$

The right member of (21), as in (9), corresponds to the Dirac result.^[4] Hence Eq. (21) allows the generalization of the result obtained above to the case of $2 < \nu < 2(2l + 1)$ electrons, assuming that λ_1 and λ_2 take on independently of each other not two, but ν values. Then, using the identity (10) twice, we obtain

$$\begin{aligned} H_{\text{ex}} &= - \sum_{n \neq m} \sum_{\lambda_n, \lambda_m} I_{n\lambda_n; m\lambda_m} S_{n\lambda_n} S_{m\lambda_m} \\ &\equiv \frac{1}{\sqrt{2}} \sum_{n \neq m} \left\{ \sum_{\lambda_n, \lambda_m} I_{n\lambda_n; m\lambda_m} S_n S_m + \sum_{\lambda_n' < \lambda_n''; \lambda_m' < \lambda_m''} (I_{n\lambda_n'; m\lambda_m'} - I_{n\lambda_n''; m\lambda_m''}) \right. \\ &\quad \left. + I_{n\lambda_n''; m\lambda_m''} - I_{n\lambda_n'; m\lambda_m''} - I_{n\lambda_n''; m\lambda_m'} \right) \\ &\quad \times A_{n\lambda_n' \lambda_n''} A_{m\lambda_m' \lambda_m''} + \sum_{\lambda_n; \lambda_m' < \lambda_m''} (I_{n\lambda_n; m\lambda_m'} - I_{n\lambda_n; m\lambda_m''}) \\ &\quad \times S_n A_{m\lambda_m' \lambda_m''} + \sum_{\lambda_n' < \lambda_n''; \lambda_m} (I_{n\lambda_n'; m\lambda_m} - I_{n\lambda_n''; m\lambda_m}) \\ &\quad \left. \times A_{n\lambda_n' \lambda_n''} S_n \right\}; \end{aligned} \quad (22)$$

$$S_n = \sum_{\lambda_n} S_{n\lambda_n}, \quad A_{n\lambda_n' \lambda_n''} = S_{n\lambda_n'} - S_{n\lambda_n''}. \quad (22)$$

⁵⁾This situation was not considered properly by Wolf, [7] who obtained the dispersion law for the para- and orthowaves in a ferromagnetic which result from our expressions for $E_{\mathbf{k}}^S$ and $E_{\mathbf{k}}^T$ if one puts

$$I_{n\alpha; m\alpha} = 0, \quad I_{n\alpha; m\beta} = I_{n\beta; m\alpha} = J_2, \quad I_{n\beta; m\beta} = J_1, \quad I_{n\alpha; n\beta} = J.$$

From (22) it is also seen that for a direct exchange interaction the "rigidity" of the spin \mathbf{S}_n depends on the magnitudes of the differences $I_{n\lambda_1; m\lambda_2} - I_{n\lambda_3; m\lambda_4}$ for all possible values $\lambda_1, \lambda_2, \lambda_3, \lambda_4$, so that only when these differences are small is the principal role played by terms of type $\mathbf{S}_n \mathbf{S}_m$, and the remaining ones can be considered as perturbations.

4. We consider now some applications of the generalized s-d exchange model. We begin by explaining how \tilde{H}_1 of (6) affects the establishment of the superconducting state. In this we shall assume, in accordance with Hund's rule, that the ground states of the transition ions are triplets and the intermediate states singlets. Then in second order of perturbation theory, \tilde{H}_1 induces an interaction of the Bardeen-Cooper-Schrieffer (BCS) electron pairs,^[8] which is described by the Hamiltonian

$$\begin{aligned} \tilde{H}_{ee} = N^{-2} \Delta^{-1} \sum_{\mathbf{k}, \mathbf{k}_1, n} \{ \tilde{J}_{\mathbf{k}, \mathbf{k}_1} \cdot 2(A_n^z)^2 \\ + \tilde{J}_{\mathbf{k}, -\mathbf{k}_1} (A_n^+ A_n^- + A_n^- A_n^+) \} b_{\mathbf{k}_1}^+ b_{\mathbf{k}}, \end{aligned} \quad (23)$$

where Δ is a positive excitation energy, equal to the energy difference of the singlet and triplet states and compared to which we have neglected the difference in the energies $E_{\mathbf{k}} - E_{\mathbf{k}_1}$ of the conduction electrons; $b_{\mathbf{k}}^+ = a_{\mathbf{k}\uparrow}^+ a_{-\mathbf{k}\downarrow}^+$ and $b_{\mathbf{k}} = a_{-\mathbf{k}\downarrow} a_{\mathbf{k}\uparrow}$ are the creation and annihilation operators respectively of a BCS pair, and $\tilde{J}_{\mathbf{k}\mathbf{k}_1} = \tilde{I}_{\mathbf{k}, \mathbf{k}_1} \tilde{I}_{-\mathbf{k}, -\mathbf{k}_1}$, where $\tilde{I}_{\mathbf{k}, \mathbf{k}_1}$ is an s-d exchange integral antisymmetric with respect to the states α and β , equal to $(1/2)(I_{\alpha, \mathbf{k}, \mathbf{k}_1, n} - I_{\beta, \mathbf{k}, \mathbf{k}_1, n})$. Considering that $\tilde{I}_{\mathbf{k}, \mathbf{k}_1} = \tilde{I}(|\mathbf{k} - \mathbf{k}_1|)$, this can also be written in the form $\tilde{J}_{\mathbf{k}\mathbf{k}_1} = \tilde{I}^2(|\mathbf{k} - \mathbf{k}_1|)$.

Transforming from BCS pairs to singlet and triplet pairs of conduction electrons with $S^Z = 0$ according to the relations^[9]

$$B_{\mathbf{k}}^S = 2^{-1/2}(b_{\mathbf{k}} + b_{-\mathbf{k}}), \quad B_{\mathbf{k}}^T = 2^{-1/2}(b_{\mathbf{k}} - b_{-\mathbf{k}}), \quad (24)$$

we obtain from (23)

$$\begin{aligned} \tilde{H}_{ee} = N^{-2} \Delta^{-1} \sum_{\mathbf{k}, \mathbf{k}_1, n} \{ \tilde{P}_{\mathbf{k}\mathbf{k}_1} [A_n^+ A_n^- + A_n^- A_n^+ + 2(A_n^z)^2] \\ \times B_{\mathbf{k}_1}^{*S} B_{\mathbf{k}}^S - \tilde{R}_{\mathbf{k}\mathbf{k}_1} [A_n^+ A_n^- + A_n^- A_n^+ - 2(A_n^z)^2] \\ \times B_{\mathbf{k}_1}^{*T} B_{\mathbf{k}}^T \}; \end{aligned} \quad (25)$$

$$\tilde{P}_{\mathbf{k}\mathbf{k}_1} = \tilde{J}_{\mathbf{k}, \mathbf{k}_1} + \tilde{J}_{-\mathbf{k}, -\mathbf{k}_1} + \tilde{J}_{\mathbf{k}, -\mathbf{k}_1} + \tilde{J}_{-\mathbf{k}, \mathbf{k}_1}, \quad (26)$$

$$\tilde{R}_{\mathbf{k}\mathbf{k}_1} = \tilde{J}_{\mathbf{k}, \mathbf{k}_1} + \tilde{J}_{-\mathbf{k}, -\mathbf{k}_1} - \tilde{J}_{\mathbf{k}, -\mathbf{k}_1} - \tilde{J}_{-\mathbf{k}, \mathbf{k}_1}, \quad (27)$$

where the prime on the summation indicates that the sum is carried out over the half-space $k_Z > 0$. Using the obvious relation

$$A_n^+ A_n^- + A_n^- A_n^+ + 2(A_n^z)^2 = 2(A_n^z)^2, \quad (28)$$

the right part of which in the $S = 1$ case we are considering equals $S(S + 1)$, we obtain from (25) the Hamiltonian for the interaction of the singlet pairs of conduction electrons:

$$\tilde{H}_{ee}^S = \frac{\zeta}{N} \frac{S(S + 1)}{\Delta} \sum'_{\mathbf{k}, \mathbf{k}_1} \tilde{P}_{\mathbf{k}\mathbf{k}_1} B_{\mathbf{k}_1}^{*S} B_{\mathbf{k}}^S, \quad (29)$$

where ζ is the concentration of transition ions. It follows from (29) and (26) that for $\tilde{J}_{\mathbf{k}\mathbf{k}_1}$ and $\Delta > 0$, the exchange of the d shells with the conduction electrons induces a repulsion of the singlet pairs of the latter at the Fermi surface and therefore precludes the establishment of superconductivity.

In the case of the triplet pairs of conduction electrons it is necessary, according to (25) and for $S = 1$ to use the relation

$$\begin{aligned} A_n^+ A_n^- + A_n^- A_n^+ - 2(A_n^z)^2 \\ = \begin{cases} S(S + 1) & \text{for } S_n^z = \pm 1 \\ -S(S + 1) & \text{for } S_n^z = 0 \end{cases}, \end{aligned} \quad (30)$$

Therefore the Hamiltonian of the interaction of the triplet pairs of the conduction electrons is

$$\tilde{H}_{ee}^T = \mp \frac{\zeta}{N} \frac{S(S + 1)}{\Delta} \sum'_{\mathbf{k}, \mathbf{k}_1} \tilde{R}_{\mathbf{k}\mathbf{k}_1} B_{\mathbf{k}_1}^{*T} B_{\mathbf{k}}^T, \quad (31)$$

where the upper sign corresponds to the cases of shells with $S_n^Z = \pm 1$, and the lower sign to shells with $S_n^Z = 0$. It follows from this, that for $\tilde{R}_{\mathbf{k}\mathbf{k}_1} > 0$, the "left" or "right" triplet states of the d shells (with $S_n^Z = \pm 1$) are energetically more favorable, and for $\tilde{R}_{\mathbf{k}\mathbf{k}_1} < 0$, the "zero" triplet states (with $S_n^Z = 0$) are.

Thus, the Hamiltonian \tilde{H}_1 can induce (in addition to the phonon attraction) an attraction of the triplet electron pairs and facilitate the establishment of a superconducting state. This is of interest in connection with explaining the experiments of Matthias and others,^[10] in which there was found an increase in the critical superconducting transition temperature T_C for titanium when traces of Cr, Mn, Fe, Co, and Ni were added to it. The Akhiezers^[11] have expressed the opinion that this increase in T_C is caused by an addition to the phonon attraction of triplet pairs of conduction electrons, of an attraction induced by their interaction with virtual ferromagnons. It is known, however, that in the case of impurity ferromagnetism,^[12-14] the Curie point is directly proportional to the concentration. Meanwhile, in the experiment of Matthias et al.^[10] the growth of T_C was observed even at low initial concentrations of impurity and at a temperature of about 1°K, which for such concentrations can perfectly well turn out to be above the Curie point, i.e., in the paramagnetic region. Besides, there is

no experimental information about the presence of ferro- or antiferromagnetism in the samples investigated in^[10]. Hence, in order to explain the results obtained in^[10] it is necessary to find a supplementary mechanism that does not depend on the presence of ferro- or antiferromagnetic ordering. Such a mechanism can be, as is clear from (31), the interaction of triplet pairs of conduction electrons induced by virtual multiplicity excitations. In this, according to (31), the superconducting state can lift the degeneracy of the triplet states of the transition ions and so regulate these states by establishing a unique ordering in the sense of a preference for states with $S_n^Z = \pm 1$ or with $S_n^Z = 0$. In both cases the total projection of the spin of all the d shells of the crystal is still equal to zero, obviously, because of the equality of states with $S_n^Z = 1$ and $S_n^Z = -1$ when there is no ferromagnetic ordering.

5. We now consider the effect of the Hamiltonian \tilde{H}_1 of (6) on the ordering of the spins of the electron system. In the first order of perturbation theory \tilde{H}_1 , unlike H_1 , does not lead to a "magnetization" of the conduction electrons due to a ferromagnetic orientation of the spins of the d shells. This is because the operator S_n^Z has diagonal elements $+1$ and -1 in the states Ψ_1^T and Ψ_{-1}^T , whereas the operator A_n^Z (and also A_n^+ and A_n^-) has them equal to zero for all four states of the table. However, the operator A_n^Z has non-zero diagonal elements $+1$ and -1 respectively for the states $2^{-1/2}(\Psi_0^S + \Psi_0^T)$ and $2^{-1/2}(\Psi_0^S - \Psi_0^T)$, which are superpositions of the states with $S = 0$ and $S = 1$. Here the wave function $2^{-1/2}(\Psi_0^S + \Psi_0^T)$ corresponds to the case when the state α has only the spin projection \uparrow and the state β only the spin projection \downarrow , whereas $2^{-1/2}(\Psi_0^S - \Psi_0^T)$ corresponds to the state when the state α has only the projection \downarrow and the state β only the projection \uparrow . In these states the diagonal terms of the Hamiltonian H' of (5) are equal to

$$H' = - \sum_{\mathbf{k}} (I_{\alpha, \mathbf{k}, \mathbf{k}} n_{\mathbf{k}\sigma} + I_{\beta, \mathbf{k}, \mathbf{k}} n_{\mathbf{k}-\sigma}), \quad (32)$$

where $\sigma = \uparrow$ for the state $2^{-1/2}(\Psi_0^S + \Psi_0^T)$ and $\sigma = \downarrow$ for the state $2^{-1/2}(\Psi_0^S - \Psi_0^T)$, and $n_{\mathbf{k}\sigma}$ is the occupation number of the electron state (\mathbf{k}, σ) .

It follows from (32) that in the case $I_{\alpha, \mathbf{k}, \mathbf{k}} \neq I_{\beta, \mathbf{k}, \mathbf{k}}$ a polarization ("magnetization") of the conduction electron spins can arise in spite of the absence of ferromagnetic ordering of the spins of the d shells. Then the preferred orientation of the projection of the spins of the conduction electrons coincides with the orientation of the projection of the spin of that state α or β whose exchange integral with the conduction electrons has the pre-

dominant value (i.e., if, for example, α has projection \uparrow and β projection \downarrow , then the conduction electrons with projection \uparrow predominate in the case $I_{\alpha, \mathbf{k}, \mathbf{k}} > I_{\beta, \mathbf{k}, \mathbf{k}}$, and the conduction electrons with spin projection \downarrow predominate in case $I_{\alpha, \mathbf{k}, \mathbf{k}} < I_{\beta, \mathbf{k}, \mathbf{k}}$). In order to reconcile this rather unusual result with the common notion that the "magnetization" of the conduction electrons arises only in the presence of ferromagnetic ordering of the d shell spins, one can say that in the case considered it is as if there were two antiparallel magnetic sublattices respectively in states α and β , each of which "magnetizes" the conduction electrons in its own direction, with the result that that "magnetization" predominates that brings about the greater exchange interaction. In this connection one can speak of a unique "subantiferromagnetism," understanding, however, that here the sites of the oriented antiparallel magnetic "sublattices" are not situated on neighboring, but on the very same sites of the crystal lattice.

Since the polarization of the spins of the conduction electrons is accompanied by a lowering of the energy of the system, it is natural to inquire which ordering of the spins of the shells is energetically more favorable—the ferromagnetic or "subantiferromagnetic." To answer this question, we note that the average value of H' of (5) over the ferromagnetic state, when, for example, all sites of the lattice have the same spin projection $S_n^Z = \pm 1$, is determined by the expression

$$H' = - \sum_{\mathbf{k}} (I_{\alpha, \mathbf{k}, \mathbf{k}} + I_{\beta, \mathbf{k}, \mathbf{k}}) n_{\mathbf{k}\uparrow}. \quad (33)$$

Correspondingly, in first order the energy of the "magnetized" conduction electrons in the ferromagnetic state is given by the equality

$$E = E_0 - 1/4 N(0) (I_{\alpha, \mathbf{k}, \mathbf{k}} + I_{\beta, \mathbf{k}, \mathbf{k}})^2, \quad (34)$$

where E_0 is the energy of the conduction electrons in the absence of "magnetization," and $N(0)$ is the density of states near the Fermi surface on one spin projection. On the other hand, the energy of the conduction electrons in the case of a "subantiferromagnetic" state has in the same order of perturbation theory, in correspondence with (32), the form

$$\tilde{E} = E_0 - 1/4 N(0) (I_{\alpha, \mathbf{k}, \mathbf{k}} - I_{\beta, \mathbf{k}, \mathbf{k}})^2. \quad (35)$$

A comparison of (34) and (35) shows that "subantiferromagnetic" ordering is energetically more favorable than ferromagnetic ordering when the condition

$$(I_{\alpha, \mathbf{k}, \mathbf{k}} - I_{\beta, \mathbf{k}, \mathbf{k}})^2 > (I_{\alpha, \mathbf{k}, \mathbf{k}} + I_{\beta, \mathbf{k}, \mathbf{k}})^2 + 4E_H/N(0), \quad (36)$$

is satisfied, where E_H is the change in the "Hund energy" in the transition from the triplet states of the d shells to the states $2^{-1/2}(\Psi_0^S \pm \Psi_0^T)$.

The criterion (36) is of some interest for the problem^[3,13] of the realization of an antiferromagnetic state as a result of indirect exchange via the conduction electrons. Actually, in calculating only the usual s-d exchange Hamiltonian H_1 , first-order perturbation theory leads to an energy advantage (at 0° K) for the "magnetization" of the conduction electrons with corresponding ferromagnetic orientation of the d-shell spins. But a calculation of the Hamiltonian \tilde{H}_1 shows, according to (36), the fundamental possibility of realizing, in this approximation, a state that is energetically more favorable than that of ferromagnetic ordering.

In the second approximation, the Hamiltonian \tilde{H}_1 leads to an interaction the reduced⁶⁾ "z part" of which has the form

$$\begin{aligned} \tilde{H}_2 = 2N^{-2} \sum_{\mathbf{k}, \mathbf{k}', n, m} |\tilde{T}_{\mathbf{k}, \mathbf{k}'}|^2 \exp [i(\mathbf{k} - \mathbf{k}')(\mathbf{R}_m - \mathbf{R}_n)] \\ \times \frac{f_{\mathbf{k}}(1 - f_{\mathbf{k}'})}{E_{\mathbf{k}} - E_{\mathbf{k}'} + \Delta_H} A_n^z A_m^z, \end{aligned} \quad (37)$$

where $f_{\mathbf{k}}$ is the Fermi distribution function for electrons with one projection of spin, which can here be taken as the same for both possible spin projections of the conduction electron, just as in the analogous relation used by Yosida,^[3] and $\Delta_H = +\Delta, -\Delta, 0$, respectively for singlet and triplet states and the superpositions $2^{-1/2}(\Psi_0^S \pm \Psi_0^T)$.

There is no contribution from \tilde{H}_2 to the energy of the state with ferromagnetic ordering of the d-shell spins, but it contains an additional interaction for the state with a non-ferromagnetic arrangement of the spins of the d-shell electrons. That is to say, setting $|\tilde{T}_{\mathbf{k}\mathbf{k}'}| \cong \tilde{T} = \text{const}$ for the states $2^{-1/2}(\Psi_0^S \pm \Psi_0^T)$ close to the Fermi surface, (37) can be brought into the form

$$\tilde{H}_2 = \left(\frac{3n_e}{2N}\right)^2 \frac{2\pi}{E_F} \tilde{T}^2 \sum_{n, m} F(2\mathbf{k}_F \mathbf{R}_{nm}) A_n^z A_m^z, \quad (38)$$

where n_e is the concentration of conduction electrons, E_F and \mathbf{k}_F are the energy and wave vector, respectively, of the Fermi surface, and the function F has the form $F(x) = (x \cos x - \sin x) x^{-4}$, as in^[3].

The appearance in (38) of the function $F(x)$ is associated with the oscillation of the density of the conduction electrons. Namely, from (6) we obtain

⁶⁾The complete expression for indirect exchange contains, just as does (20), products of the type $S_n S_m, A_n A_m, A_n S_m,$ and $S_n A_m$. Equation (37) includes only that part of the interaction that is of interest to us at this point.

an oscillating correction in first order for the density of the conduction electrons:

$$\delta\rho_\sigma = \mp 2N^{-1} \sum_{\mathbf{k}} \sum_{\mathbf{k}'(\neq\mathbf{k})} \frac{\tilde{T}_{\mathbf{k}, \mathbf{k}'}}{E_{\mathbf{k}} - E_{\mathbf{k}'}} \sum_n A_n^z \cos [(\mathbf{k} - \mathbf{k}')(\mathbf{R}_n - \mathbf{r})], \quad (39)$$

where the upper sign belongs to the case $\sigma = 1$, and the lower sign to $\sigma = -1$. Clearly, these oscillations caused by the "unusual" Hamiltonian do not occur when the states $\Psi_0^S, \Psi_0^T, \Psi_1^T$, or Ψ_{-1}^T , in which the diagonal elements of the operator A_n^z are zero, are filled in the d shells. However, these oscillations can occur in the realization in the d shells of a "subantiferromagnetic" state, since the superpositions $2^{-1/2}(\Psi_0^S \pm \Psi_0^T)$ are eigenfunctions of the operator A_n^z corresponding to the eigenvalues ± 1 .

6. In conclusion we remark that the expansion used in this paper for the exchange interaction, a sum of terms of the form

$$^{1/2}(I_\alpha + I_\beta)(S_\alpha + S_\beta) + ^{1/2}(I_\alpha - I_\beta)(S_\alpha - S_\beta) \quad (40)$$

is formally analogous to the representation of the spin part of the magnetic moment of the deuteron in the form^[15]

$$^{1/2}(\mu_n + \mu_p)(S_n + S_p) + ^{1/2}(\mu_n - \mu_p)(S_n - S_p),$$

where μ_n, S_n , and μ_p, S_p are the magnetic moments and spin operators of the neutron and proton, respectively. The A operator of the given paper that is contained in the last term has, as is well known, significant value for the elucidation of the triplet-singlet transitions of the deuteron (due to radiation processes, e.g., in the radiation trapping of a neutron by a proton), the ortho and para molecules of hydrogen,^[16] etc. This analogy, as well as other considerations, suggests that the results set forth above might be generalized to questions of the structure, superflow, and spin ordering of a nuclear material.

APPENDIX

The creation operators for the singlet and triplet states are defined via the second quantization operators in the following way:

$$\begin{aligned} B_n^{*S} &= 2^{-1/2}(a_{n\alpha\uparrow}^* a_{n\beta\downarrow}^* - a_{n\alpha\downarrow}^* a_{n\beta\uparrow}^*), \\ B_n^{*T} &= 2^{-1/2}(a_{n\alpha\uparrow}^* a_{n\beta\downarrow}^* + a_{n\alpha\downarrow}^* a_{n\beta\uparrow}^*), \quad S^z = 0, \\ B_{n\sigma}^* &= a_{n\alpha\sigma}^* a_{n\beta\sigma}^*, \quad S^z = \pm 1, \quad \sigma = \uparrow, \downarrow. \quad (A-1) \end{aligned}$$

Using (A-1), it is not difficult to establish the following connection between these operators and the operators that appear in developing the sums over σ_1, σ_2 , and λ in the Hamiltonian (3):

$$a_{n\lambda\sigma}^* a_{n\lambda\sigma} \rightarrow \pm ^{1/2}(B_n^{*S} B_n^T + B_n^{*T} B_n^S) + [^{1/2}(B_n^{*S} B_n^S$$

$$\begin{aligned}
& + B_n {}^*T B_n^T + B_{n\sigma} {}^*B_{n\sigma}], \\
a_{n\lambda\downarrow}^* a_{n\lambda\uparrow} & \rightarrow \pm 2^{-1/2} (B_{n\downarrow} {}^*B_n^S - B_n {}^*S B_{n\uparrow}) \\
& + 2^{-1/2} (B_{n\downarrow} {}^*B_n^T + B_n {}^*T B_{n\uparrow}), \quad (A-2)
\end{aligned}$$

where the upper sign before the first parenthesis in each expression is used for $\lambda = \alpha$, and the lower for $\lambda = \beta$ (the upper formula is written for $\sigma = \uparrow$; in case $\sigma = \downarrow$ the signs before the first parenthesis change places). From (A-2) and (3) follows:

$$\begin{aligned}
H' & = -N^{-1} \sum_{\mathbf{k}, \mathbf{k}', n} \frac{1}{2} (I_{\alpha, \mathbf{k}, \mathbf{k}', n} - I_{\beta, \mathbf{k}, \mathbf{k}', n}) \\
& \times \{ (B_n {}^*S B_n^T + B_n {}^*T B_n^S) (a_{\mathbf{k}'\uparrow}^* a_{\mathbf{k}\uparrow} - a_{\mathbf{k}'\downarrow}^* a_{\mathbf{k}\downarrow}) + \sqrt{2} \\
& \times (B_{n\downarrow} {}^*B_n^S - B_n {}^*S B_{n\uparrow}) a_{\mathbf{k}'\uparrow}^* a_{\mathbf{k}\downarrow} \\
& + \sqrt{2} (B_n {}^*S B_{n\downarrow} - B_{n\uparrow} {}^*B_n^S) a_{\mathbf{k}'\downarrow}^* a_{\mathbf{k}\uparrow} \} \\
& - N^{-1} \sum_{\mathbf{k}, \mathbf{k}', n} \frac{1}{2} (I_{\alpha, \mathbf{k}, \mathbf{k}', n} + I_{\beta, \mathbf{k}, \mathbf{k}', n}) \\
& \times \{ (B_n {}^*S B_n^S + B_n {}^*T B_n^T + 2B_{n\uparrow} {}^*B_{n\uparrow}) a_{\mathbf{k}'\uparrow}^* a_{\mathbf{k}\uparrow} \\
& + (B_n {}^*S B_n^S + B_n {}^*T B_n^T + 2B_{n\downarrow} {}^*B_{n\downarrow}) a_{\mathbf{k}'\downarrow}^* a_{\mathbf{k}\downarrow} \\
& + \sqrt{2} (B_{n\downarrow} {}^*B_n^T + B_n {}^*T B_{n\uparrow}) a_{\mathbf{k}'\uparrow}^* a_{\mathbf{k}\downarrow} \\
& + \sqrt{2} (B_{n\uparrow} {}^*B_n^T + B_n {}^*T B_{n\downarrow}) a_{\mathbf{k}'\downarrow}^* a_{\mathbf{k}\uparrow} \}. \quad (A-3)
\end{aligned}$$

It is not difficult to see that

$$\begin{aligned}
B_n {}^*S B_n^S + B_n {}^*T B_n^T + 2B_{n\uparrow} {}^*B_{n\uparrow} & = 1 + S_n^z, \\
B_n {}^*S B_n^S + B_n {}^*T B_n^T + 2B_{n\downarrow} {}^*B_{n\downarrow} & = 1 - S_n^z, \\
\sqrt{2} (B_{n\downarrow} {}^*B_n^T + B_n {}^*T B_{n\uparrow}) & = S_n^-, \\
\sqrt{2} (B_{n\uparrow} {}^*B_n^T + B_n {}^*T B_{n\downarrow}) & = S_n^+, \quad (A-4)
\end{aligned}$$

where $S_n = S_n\alpha + S_n\beta$. Introducing now the symbols

$$\begin{aligned}
B_n {}^*S B_n^T + B_n {}^*T B_n^S & = A_n^z, \\
\sqrt{2} (B_{n\downarrow} {}^*B_n^S - B_n {}^*S B_{n\uparrow}) & = A_n^-, \\
\sqrt{2} (B_n {}^*S B_{n\downarrow} - B_{n\uparrow} {}^*B_n^S) & = A_n^+, \quad (A-5)
\end{aligned}$$

we obtain Eq. (6) from (A-3), (A-4), and (A-5). It is not difficult to show that the operators defined

in (A-5) act on the wave functions of the singlet and triplet states in the manner indicated in the table.

¹S. V. Vonsovskii, JETP 16, 981 (1946); S. V. Vonsovskii and E. A. Turov, JETP 24, 419 (1953).

²T. Kasuya, Progr. Theoret. Phys. (Kyoto) 16, 45 (1956).

³K. Yosida, Phys. Rev. 106, 893 (1957).

⁴P. A. M. Dirac, The Principles of Quantum Mechanics, Oxford, Clarendon Press, 1958 (Russ. Transl., M., 1960, p. 309).

⁵N. N. Bogolyubov, Lektsii po kvantovoi statistike (Lectures in Quantum Statistics), Kiev, 1949.

⁶S. P. Shubin and S. V. Vonsovskii, Physik. Z. Sowjetunion 7, 322 (1935).

⁷A. Wolf, Z. Physik 70, 519 (1931).

⁸Bardeen, Cooper, and Schrieffer, Phys. Rev. 108, 1175 (1957).

⁹S. V. Vonsovskii and M. S. Svirskii, JETP 46, 1619 (1964), Soviet Phys. JETP 19, 1095 (1964); Izv. AN SSSR, ser. fiz., 28, 419 (1964), Columbia Tech. Transl. in press.

¹⁰Matthias, Compton, Suhl, and Corenzwit, Phys. Rev. 115, 1597 (1959).

¹¹A. I. Akhiezer and I. A. Akhiezer, JETP 43, 2208 (1962), Soviet Phys. JETP 16, 1560 (1963).

¹²S. H. Liu, Phys. Rev. 123, 470 (1961).

¹³A. A. Abrikosov and A. P. Gor'kov, JETP 43, 2230 (1962), Soviet Phys. JETP 16, 1575 (1963).

¹⁴S. V. Vonsovskii and M. S. Svirskii, FMM 15, 316 (1963).

¹⁵Sb. Stroenie atomnogo yadra (Collection, Structure of the Atomic Nucleus), IIL, 1959.

¹⁶A. Akhiezer and I. Pomeranchuk, Nekotorye voprosy teorii yadra (Some Questions on the Theory of the Nucleus), M.-L., 1948, pp. 38, 69.

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