

A "SOLUBLE" CASE OF BOUND STATES OF CONDUCTION ELECTRONS AND
MAGNETIC IMPURITY ATOMS

A. A. ABRIKOSOV

Institute of Theoretical Physics, U.S.S.R. Academy of Sciences

Submitted June 19, 1967

Zh. Eksp. Teor. Fiz. 53, 2109-2122 (December 1967)

We consider the problem of bound states when the spin of the impurity atom is unity. In that case, the "parquet" equation for the state amplitude^[1] degenerates into a "chain." As a result we get for a number of quantities - the amplitudes themselves, the critical temperature, the specific heat, and magnetic characteristics - solutions without unknown constants. This makes it possible to analyze the temperature dependence of the main properties.

IN a previous paper^[1] we showed that in the case when there are magnetic impurity atoms in a non-magnetic metal and when the sign of the exchange interaction between the conduction electrons and the impurity spins is antiferromagnetic, bound states of the conduction electrons and the impurity spin may occur. This is a collective effect and the state formed is much closer to a Cooper pair in a superconductor than to a normal bound state such as an atom. We obtained in^[1] a "parquet" type of equation for the state amplitude and it is difficult to solve this equation completely. The equation was solved with logarithmic accuracy and the amplitude was determined with an unknown constant factor. Since the factor in principle could be equal to zero, the problem could not be considered to be finally solved.

It was already noted in^[1] that the amplitude $\Delta(\omega)$ as a function of the energy ω increases with decreasing ω when the impurity spin $S = 1/2$, decreases when $S \geq 3/2$, and is constant when $S = 1$. The case $S = 1$ is thus a distinct one and the problem arises whether the "parquet" here would not turn into a simple chain as in the superconductivity case. In fact, in the latter case $\Delta = \text{const}$ when $\omega \ll \omega_D$ (Debye frequency). We show in the following that this is indeed the case for $S = 1$. As a result the equations simplify and one can solve them completely. One can also find the thermodynamic and magnetic properties of such systems.

The results are partially the same as those obtained by Nagaoka.^[2,3] As we noted already in^[1], Nagaoka's method has no rigorous foundation and is clearly not applicable for $S \neq 1$. In his method the case $S = 1$ is not at all a special one. The results obtained by him are therefore also for $S = 1$ open to doubt. We shall show below that most of Nagaoka's results are incorrect.

1. CALCULATION METHOD. SINGULARITY OF SCATTERING AMPLITUDE

We showed in the Appendix to^[1] that in the case $S = 1$ one can use a calculation technique based upon the substitution

$$\hat{S}^i = a_{\beta^+} S_{\beta\beta'}^i a_{\beta} \quad (1)$$

without introducing an energy $\lambda \gg T$ for each pseudoparticle corresponding to the operator a_{β} . This is a very valuable circumstance. The Green function of a

free pseudoparticle has the form

$$\mathcal{G}_{\beta\beta'} = -\text{Sp} \langle T(a_{\beta}(\tau) a_{\beta'}(\tau')) \rangle = T \sum_{\omega_n} \mathcal{G}_{\beta\beta'}(\omega_n) \exp[-i\omega_n(\tau - \tau')],$$

$$\mathcal{G}_{\beta\beta'}(\omega_n) = 1 / i\omega_n, \quad \omega_n = \pi T(2n + 1). \quad (2)$$

The trace is here taken over all states including the "unphysical" ones. We use here the fact that the operators a_{β} and a_{β}^+ occur only in the combinations (1), which give zero when acting upon unphysical states, in all physical quantities. The only thing which one must do here is to introduce a normalizing factor.

We assume that we average a physical quantity $\hat{\mathcal{A}}$ which is a time-ordered product of components of the spin of the given atom. We have (see^[4], Sec. 12)

$$\bar{\mathcal{A}} = \text{Sp}_{\text{phys}} \{ e^{-\mathcal{H}/T} \hat{\mathcal{A}} \} / \text{Sp}_{\text{phys}} \{ e^{-\mathcal{H}/T} \}.$$

The trace must here be taken only over physical states but by virtue of the property (1) of the operators mentioned above we may assume that in the numerator it is taken over all states. In the denominator it is no longer possible to change to a trace over all states. However, in order to get rid of the unconnected diagrams in the evaluation of $\bar{\mathcal{A}}$ (see^[4]), it is necessary that the trace is taken over a complete set of states. Because of this we can evaluate $\bar{\mathcal{A}}$ by the usual rules but afterwards divide the average obtained by the ratio

$$Q = \text{Sp}_{\text{phys}} \{ e^{-\mathcal{H}/T} \} / \text{Sp} \{ e^{-\mathcal{H}/T} \}.$$

We consider now the average

$$\langle \hat{S}^2 \rangle = \text{Sp} \{ e^{-\mathcal{H}/T} \hat{S}^2 \} / \text{Sp} \{ e^{-\mathcal{H}/T} \},$$

where the trace is taken over all states. It is clear that in the numerator only physical states take part and acting upon them \hat{S}^2 gives $S(S + 1) = 2$. We have thus¹⁾

$$Q = \frac{\text{Sp}_{\text{phys}} \{ e^{-\mathcal{H}/T} \}}{\text{Sp} \{ e^{-\mathcal{H}/T} \}} = \frac{\langle \hat{S}^2 \rangle}{2}. \quad (3)$$

Thus

$$\bar{\mathcal{A}} = \langle \mathcal{A} \rangle / Q, \quad (4)$$

where $\langle \mathcal{A} \rangle$ and $\langle \hat{S}^2 \rangle$ which occur in Q are evaluated by the usual rules of the diagram technique. When

¹⁾If we substitute (1) we can verify that when $S = 1$, the quantity $\hat{S}^2 \equiv \hat{N}(3 - \hat{N})$, where $\hat{N} = \sum_{\beta} a_{\beta}^{\dagger} a_{\beta}$.



FIG. 1



FIG. 2

there are no bound states we get

$$Q = 1 - \frac{1}{4} \operatorname{sech}^2 \frac{g\mu H}{2T}, \quad (5)$$

i.e., $Q \rightarrow 3/4$ when $g\mu H \ll T$ and $Q \rightarrow 1$ when $g\mu H \gg T$. We give the evaluation of Q when there are bound states in the Appendix.

We shall now show similarly to Sec. 33 of [4] that at some temperature there arises a singularity in one of the vertex parts. We consider the case $H = 0$. We note first of all that as the Hamiltonian contains the total spin of the system one can classify the states according to the total spin of the electron plus impurity. When $I = S + 1/2$ we have $\sigma S = S$, and when $I = S - 1/2$ we get $\sigma S = -(S + 1)$. We consider two basic singular diagrams in the vertex part (Fig. 1). The diagram of Fig. 1b contains the factor $\sigma^i \sigma^k \sigma^i \sigma^k = S(S + 1) + \sigma S$. In the state $I = S - 1/2$ this factor vanishes when $S = 1$. As to the diagram of Fig. 1a it contains a factor $S(S + 1) - \sigma S$ and does not vanish. Because of this we can to logarithmic accuracy restrict ourselves when evaluating the vertex part to summing the chain of Fig. 2 instead of the "parquet" (see [5]).

We are, however, interested in the problem whether it is possible to evaluate the vertex part more accurately. For this purpose we investigate what happens when we make the "nucleus" more complicated in the chain of Fig. 2. The first correction consists in the substitution illustrated in Fig. 3a but as the diagram of Fig. 1 vanishes exactly, the first correction to the "nucleus" does not contribute. The next order are the diagrams of Figs. 3b, c, d. Giving not a simple, but a lengthy estimate we show merely that then we must add to $\omega J/N$ a quantity of order $(\omega J/N)^3$ (where $\alpha = p_0 m / 2\pi^2$, J is the exchange interaction constant, and N the density of atoms in the basic metal). The corrections which may be of interest to us are $(\omega J/N)^3 \ln(\epsilon_F / \omega), \dots$. The situation is similar for higher order and "non-parquet" diagrams. For example, the diagram of Fig. 3e adds to $\omega J/N$ a quantity of order $(\omega J/N)^4 \ln(\epsilon_F / \omega)$. Thus, even in the case when we wish to find the pole with non-logarithmic accuracy it is sufficient for us, for $S = 1$, to sum the chain of Fig. 2 with a simple nucleus.

Putting the total frequency at the ends equal to zero we get for each link

$$\begin{aligned} -T\alpha \sum_{\omega} \int_{-\Lambda}^{\Lambda} d\xi \frac{1}{i\omega - i\omega - \xi} &= -2T\alpha \sum_{\omega > 0} \int_{-\Lambda}^{\Lambda} d\xi \frac{1}{\omega^2 + \xi^2} \\ &= -\alpha \int_0^{\Lambda} \frac{\xi d\xi}{2T \xi} = -\alpha \ln \frac{2\gamma\Lambda}{\pi T}, \end{aligned}$$

where $\gamma = e^C = 1.78$, $\Lambda \sim \epsilon_F$. Summing the whole chain, we get

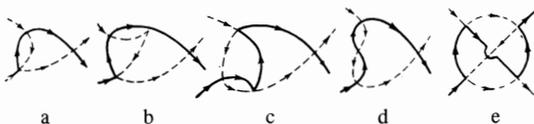


FIG. 3

$$\Gamma_{S=1/2} = -2 \frac{J}{N} \left[1 + 2 \frac{J}{N} \alpha \ln \frac{2\gamma\Lambda}{\pi T} \right]. \quad (6)$$

If $J < 0$, this expression becomes infinite when

$$T_c = \frac{2\gamma\Lambda}{\pi} \exp\left\{-\frac{N}{2\alpha|J|}\right\}. \quad (7)$$

This shows, unconditionally, the possibility to form bound states for $S = 1$ and makes it very probable that the same is the case when $S \neq 1$.

2. AMPLITUDE OF THE BOUND STATE

As in [1], we introduce basic functions, but here they refer to the temperature-dependent technique:

$$\begin{aligned} G_{\alpha\alpha'} &= -\langle T(\psi_{\alpha}(x)\psi_{\alpha'}(x')) \rangle, \quad F_{\alpha\beta}^{(2)} = \langle T(\psi_{\alpha}^{+}(x)a_{\beta n}^{+}(\tau')) \rangle, \\ \mathcal{G}_{\beta\beta', nm} &= -\langle T(a_{n\beta}^{+}(\tau)a_{m\beta'}(\tau')) \rangle, \quad F_{\alpha\beta}^{(3)} = \langle T(\psi_{\alpha}(x)a_{\beta n}^{+}(\tau')) \rangle, \\ D_{\alpha\alpha'} &= -\langle T(\psi_{\alpha}(x)\psi_{\alpha'}(x')) \rangle, \quad F_{\alpha\beta}^{(4)} = \langle T(\psi_{\alpha}^{+}(x)a_{\beta n}(\tau')) \rangle, \\ D_{\alpha\alpha'}^{+} &= \langle T(\psi_{\alpha}^{+}(x)\psi_{\alpha'}(x')) \rangle, \quad \Delta_{\alpha\beta}^{(1)} = \frac{J}{N} \sigma_{\alpha\alpha'}^i S_{\beta\beta'}^i F_{\alpha'\beta'}^{(1)}(\mathbf{r}_n\tau, \mathbf{r}_n\tau), \\ \mathcal{D}_{\beta\beta', nm} &= -\langle T(a_{n\beta}(\tau)a_{m\beta'}(\tau')) \rangle, \quad \Delta_{\alpha\beta}^{(2)} = \frac{J}{N} \sigma_{\alpha'\alpha}^i S_{\beta\beta'}^i F_{\alpha'\beta'}^{(2)}(\mathbf{r}_n\tau, \mathbf{r}_n\tau), \\ \mathcal{D}_{\beta\beta', nm}^{+} &= \langle T(a_{n\beta}(\tau)a_{m\beta'}^{+}(\tau')) \rangle, \quad \Delta_{\alpha\beta}^{(3)} = \frac{J}{N} \sigma_{\alpha\alpha'}^i S_{\beta\beta'}^i F_{\alpha'\beta'}^{(3)}(\mathbf{r}_n\tau, \mathbf{r}_n\tau), \\ F_{\alpha\beta}^{(1)} &= \langle T(\psi_{\alpha}(x)a_{\beta n}(\tau')) \rangle, \quad \Delta_{\alpha\beta}^{(4)} = \frac{J}{N} \sigma_{\alpha'\alpha}^i S_{\beta\beta'}^i F_{\alpha'\beta'}^{(4)}(\mathbf{r}_n\tau, \mathbf{r}_n\tau). \end{aligned} \quad (8)$$

The averaging for the operators a is taken over a complete set of states. Expressions such as (8) were in [1] defined only to first order in $\Delta_{\alpha\beta}^{(1)}$. However, in our case this definition is complete because of the degeneracy of the "parquet." The "zero" Green functions have the form (right from the start we shall take the magnetic field into account, M is the magnetic quantum number)

$$G^{(0)}(\omega, \xi) = \frac{1}{i\omega + \mu H \sigma_z - \xi}, \quad \mathcal{G}_{MM}^{(0)} = \frac{1}{i\omega + \mu g H M}. \quad (9)$$

The interaction Hamiltonian, described in terms of Δ is equal to

$$\begin{aligned} \mathcal{H}_{int} &= \mathcal{H}_{int,1} + \mathcal{H}_{int,2}, \\ \mathcal{H}_{int,1} &= \sum_n [\Delta_{\alpha\beta}^{(2)} \psi_{\alpha}(\mathbf{r}_n) a_{\beta n} + \Delta_{\alpha\beta}^{(1)} \psi_{\alpha}^{+}(\mathbf{r}_n) a_{\beta n}^{+} \\ &\quad - \Delta_{\alpha\beta}^{(4)} \psi_{\alpha}(\mathbf{r}_n) a_{\beta n}^{+} - \Delta_{\alpha\beta}^{(3)} \psi_{\alpha}^{+}(\mathbf{r}_n) a_{\beta n}], \\ \mathcal{H}_{int,2} &= -\frac{J}{N} \sum_n \psi_{\alpha}^{+}(\mathbf{r}_n) a_{\beta n}^{+} a_{\beta' n} \psi_{\alpha'}(\mathbf{r}_n) \sigma_{\alpha\alpha'}^i S_{\beta\beta'}^i. \end{aligned} \quad (10)$$

We have implied that ψ and a occurring in one of the $\mathcal{H}_{int,2}$ are not paired in $\Delta_{\alpha\beta}^{(1)}$. The Hamiltonian $\mathcal{H}_{int,2}$ characterizes scattering effects and does not play an important role in thermodynamics. This will be discussed in Sec. 3. However, even in those cases when it is important (e.g., for the electrical conductivity) we shall to begin with consider the affects arising from $\mathcal{H}_{int,1}$ because it is there possible to sum completely all corrections.

Thus, taking only $\mathcal{H}_{int,1}$ into account, we get an equation for G (cf. [1]):

$$\begin{aligned} G_{\alpha\alpha'}(\mathbf{r}, \mathbf{r}', \omega) &= G_{\alpha\alpha'}^{(0)}(\mathbf{r} - \mathbf{r}', \omega) \\ &+ \sum_n G_{\alpha\alpha'}^{(0)}(\mathbf{r} - \mathbf{r}_n, \omega) [\Delta_{\alpha\beta}^{(1)} \mathcal{G}_{\beta\beta'}^{(0)}(-\omega) \Delta_{\alpha\beta}^{(2)} \\ &\quad - \Delta_{\alpha\beta}^{(3)} \mathcal{G}_{\beta\beta'}^{(0)}(\omega) \Delta_{\alpha\beta}^{(4)}] G_{\alpha\alpha'}(\mathbf{r}_n, \mathbf{r}', \omega) \end{aligned}$$

$$+ \sum_n G_{\alpha\alpha}^{(0)}(\mathbf{r} - \mathbf{r}_n, \omega) [\Delta_{\alpha,\beta}^{(1)} \mathcal{G}_{\beta\beta}^{(0)}(-\omega) \Delta_{\alpha,\beta}^{(3)} - \Delta_{\alpha,\beta}^{(3)} \mathcal{G}_{\beta\beta}^{(0)}(\omega) \Delta_{\alpha,\beta}^{(1)}] D_{\alpha,\alpha'}^+ (\mathbf{r}_n, \mathbf{r}', \omega). \quad (11)$$

First of all we consider what restrictions are imposed upon the choice of Δ . It follows from (8) that

$$\Delta_{\alpha\beta}^{(2)} = -\Delta_{\alpha\beta}^{(1)*}, \quad \Delta_{\alpha\beta}^{(4)} = -\Delta_{\alpha\beta}^{(3)*}. \quad (12)$$

Moreover, only those $\Delta_{\alpha\beta}$ which correspond to the formation or destruction of a bound state with total spin $1/2$ are non-vanishing. For $\Delta_{\alpha\beta}^{(1)}$ these are $\Delta_{1/2-1}^{(1)}$,

$\Delta_{1/2 0}^{(1)}$, $\Delta_{-1/2 1}^{(1)}$, and $\Delta_{-1/2 0}^{(1)}$. Correspondingly we have for $\Delta_{\alpha\beta}^{(3)}$: $\Delta_{1/2-1}^{(3)}$, $\Delta_{-1/2-1}^{(3)}$, $\Delta_{1/2 0}^{(3)}$ and $\Delta_{-1/2 0}^{(3)}$. We noted

already in [1] that there is in this problem symmetry between electrons and holes. It is therefore natural to assume $\Delta_{1/2-1}^{(1)} = C_1 \Delta_{1/2 1}^{(3)}$, $\Delta_{-1/2 0}^{(1)} = C_2 \Delta_{-1/2 0}^{(3)}$ and similarly for the other components; C_1, C_2, \dots are here phase factors.

We now choose C_1, C_2, \dots in such a way that in Eq. (11) the coefficient of D^+ vanishes, i.e.,

$$\begin{aligned} & \Delta_{1/2-1}^{(1)} \mathcal{G}_{-1-1}^{(0)}(-\omega) \Delta_{-1/2-1}^{(3)} + \Delta_{1/2 0}^{(1)} \mathcal{G}_{00}^{(0)}(-\omega) \Delta_{-1/2 0}^{(3)} \\ & - \Delta_{1/2 1}^{(3)} \mathcal{G}_{11}^{(0)}(\omega) \Delta_{-1/2 1}^{(1)} - \Delta_{1/2 0}^{(3)} \mathcal{G}_{00}^{(0)}(\omega) \Delta_{-1/2 0}^{(1)} \\ & = -[\Delta_{1/2-1}^{(1)} \Delta_{-1/2-1}^{(3)} + \Delta_{1/2 0}^{(1)} \Delta_{-1/2 0}^{(3)}] \frac{1}{i\omega + \mu g H} \\ & - [\Delta_{1/2 0}^{(1)} \Delta_{-1/2 0}^{(3)} + \Delta_{1/2 1}^{(1)} \Delta_{-1/2 1}^{(3)}] \frac{1}{i\omega} = 0, \end{aligned}$$

and similarly for the $(-1/2, 1/2)$ coefficient.

We make the following choice:

$$\begin{aligned} \Delta_{1/2-1}^{(1)} = \Delta_{1/2 1}^{(3)} = \Delta_{-1/2 1}^{(1)} = -\Delta_{-1/2-1}^{(3)} = \delta_1, \\ \Delta_{1/2 0}^{(1)} = \Delta_{1/2 0}^{(3)} = \Delta_{-1/2 0}^{(1)} = -\Delta_{-1/2 0}^{(3)} = \delta_0. \end{aligned} \quad (13)$$

For this choice the coefficient of D^+ vanishes indeed.

We shall see below that Eq. (13) also satisfies the equation for Δ .

Equation (11) now becomes the equation for the interaction of an electron with a point impurity. The Born amplitude corresponds to

$$U(\omega) = [\Delta_{\alpha,\beta}^{(1)} \mathcal{G}_{\beta\beta}^{(0)}(-\omega) \Delta_{\alpha,\beta}^{(2)} - \Delta_{\alpha,\beta}^{(3)} \mathcal{G}_{\beta\beta}^{(0)}(\omega) \Delta_{\alpha,\beta}^{(4)}] = 2[\delta_0^2/i\omega + \delta_1^2/(i\omega + g\mu H\sigma_z)]. \quad (14)$$

We have used here Eqs. (9) and (13). The total scattering amplitude is equal to

$$V(\omega) = U(\omega) + U^2(\omega) \int G(\omega) a d\xi + U^3(\omega) \left[\int G(\omega) a d\xi \right]^2 + \dots$$

Assuming that $\int G d\xi = -i\pi\alpha \text{sign } \omega$, we find

$$V(\omega) = \frac{U(\omega)}{1 + i\pi\alpha \text{sign } \omega U(\omega)}. \quad (15)$$

The complete Green function has the form

$$G = [i\omega + \mu H\sigma_z - \xi - Q^{-1} N_i V(\omega)]^{-1} \quad (16)$$

(with allowance for the normalization $1/Q$). From this it is clear that, indeed,

$$\alpha \int G(\omega) d\xi = -i\pi\alpha \text{sign } \omega.$$

The Green function which has one end at an impurity starts with the usual G but at its end can interact an arbitrary number of times with the impurity. One sees easily that this gives

$$G^i = G[1 + i\pi\alpha \text{sign } \omega U(\omega)]^{-1}. \quad (17)$$

In particular, if both ends of G coincide at one and the same impurity, we have

$$G^i(\omega, 0, 0) = \frac{-i\pi\alpha \text{sign } \omega}{1 + i\pi\alpha \text{sign } \omega U(\omega)}. \quad (18)$$

The function $F^{(2)}$ with coordinates in one impurity atom is equal to

$$F_{\alpha\beta}^{(2)}(0, 0, 0) = \left[\frac{i\pi\alpha \text{sign } \omega}{1 - i\pi\alpha \text{sign } \omega U(-\omega)} \right]_{\alpha\alpha} \Delta_{\alpha,\beta}^{(2)} \mathcal{G}_{\beta,\beta}^{(0)}. \quad (19)$$

From Eq. (18) we find for $\Delta_{\alpha\beta}^{(2)}$

$$\begin{aligned} \Delta_{1/2-1}^{(2)} &= -\frac{J}{N} T \sum_{\omega} F_{1/2-1}^{(2)}(0, 0, 0) + \frac{J}{N} \sqrt{2} T \sum_{\omega} F_{-1/2 0}^{(2)}(0, 0, \omega), \\ \Delta_{-1/2 0}^{(2)} &= -\frac{J}{N} \sqrt{2} T \sum_{\omega} F_{1/2-1}^{(2)}(0, 0, \omega). \end{aligned} \quad (20)$$

Substituting here (19), (13), and (12), assuming $\Delta_{\alpha\beta}^{(i)}$ to be real and introducing the definition

$$\begin{aligned} \mathcal{A} &= -\frac{J}{N} T \sum_{\omega} \frac{i\pi\alpha \text{sign } \omega}{i\omega - g\mu H} \left[1 + 2i\pi\alpha \text{sign } \omega \left(\frac{\delta_0^2}{i\omega} + \frac{\delta_1^2}{i\omega - g\mu H} \right) \right]^{-1}, \\ B &= -\frac{J}{N} T \sum_{\omega} \frac{i\pi\alpha \text{sign } \omega}{i\omega} \left[1 + 2i\pi\alpha \text{sign } \omega \left(\frac{\delta_0^2}{i\omega} + \frac{\delta_1^2}{i\omega + g\mu H} \right) \right]^{-1}, \end{aligned} \quad (21)$$

we get

$$\delta_0 = -\sqrt{2} \mathcal{A} \delta_1, \quad \delta_1 = \mathcal{A} \delta_1 - \sqrt{2} B \delta_0. \quad (22)$$

Putting the determinant equal to zero we have

$$\mathcal{A}(1 + 2B) = 1. \quad (23)$$

Writing equations similar to (20) for the other components of $\Delta_{\alpha\beta}^{(2)}$ or for $\Delta_{\alpha\beta}^{(3)}$ one can verify that the assumed form of solution (13) satisfies the equations. Equation (23) determines δ_0 and δ_1 apart from the sign. According to (22) only one sign is arbitrary. In the case $H = 0$ we shall have $\mathcal{A} = B = 1/2$, $\delta_0 = -\delta_1/\sqrt{2}$ and for $J < 0$ we have

$$4\pi\alpha \left| \frac{J}{N} \right| T \sum_{\omega > 0} \frac{1}{\omega + 3\pi\alpha\delta_1^2} = 1. \quad (24)$$

3. BASIC THERMODYNAMIC CHARACTERISTICS

We first of all consider δ_1 for $H = 0$. We get for $\delta_1 = 0$ from Eq. (24) the critical temperature

$$T_c = \frac{2\Lambda\gamma}{\pi} \exp \left\{ -\frac{N}{2a|J|} \right\}.$$

This expression is the same as (7). On the other hand, assuming $T \rightarrow 0$, we change from a sum to an integral and find

$$3\pi\alpha\delta_1^2(0) = \Lambda \exp \{-N/2a|J|\}. \quad (25)$$

It follows from (25) that

$$3\pi\alpha\delta_1^2(0) = \frac{\pi}{2\gamma} T_c = \frac{T_c}{1.13}. \quad (26)$$

We can write Eq. (24) in the form of an integral, using the tanh function to go from imaginary to real ω . This gives

$$2a \left| \frac{J}{N} \right| \int_0^{\Lambda} \frac{\omega \text{th}(\omega/2T)}{\omega^2 + R^2} d\omega = 1, \quad (27)$$

where R denotes $3\pi\alpha\delta_1^2$.

We can write Eq. (24) also in another form. Adding and subtracting from the sum over ω its value at $R = 0$, we get

$$\ln \frac{T_c}{T} = \psi \left(\frac{R}{2\pi T} + \frac{1}{2} \right) - \psi \left(\frac{1}{2} \right), \quad (28)$$

where $\psi(x)$ is the logarithmic derivative of the gamma-function. Near T_c , i.e., for small R , we find from this

$$R = 1.27(T_c - T) - 0.2(T_c - T)^2/T_c. \quad (29)$$

It is convenient to use Eq. (27) near $T = 0$. From it we find for $T \ll T_c$

$$R = R(0) - \frac{\pi^2 T^2}{6R(0)} + \frac{3\pi^4 T^4}{40R^3(0)}, \quad (30)$$

where $R(0)$ is given by Eq. (26).

Nagaoka^[2] found the results (7) and (25) to (30) for arbitrary S . However, as we noted already earlier, his method is open to doubt. The derivation given here validates these results only for $S = 1$.

Let us now find the critical field. To do this we use Eqs. (21) and (23). For $\delta_1 = \delta_0 = 0$ we get from (21)

$$\begin{aligned} A &= 2\pi\alpha \left| \frac{J}{N} \right| T \sum_{\omega>0} \frac{\omega}{\omega^2 + (g\mu H_c)^2} = \frac{1}{2} + \alpha \left| \frac{J}{N} \right| \left[\ln \frac{T_c}{T} \right. \\ &\left. + \psi \left(\frac{1}{2} \right) - \frac{1}{2} \psi \left(\frac{1}{2} - \frac{ig\mu H_c}{2\pi T} \right) - \frac{1}{2} \psi \left(\frac{1}{2} + \frac{ig\mu H_c}{2\pi T} \right) \right], \\ B &= 2\pi\alpha \left| \frac{J}{N} \right| T \sum_{\omega>0} \frac{1}{\omega} = \frac{1}{2} + \alpha \left| \frac{J}{N} \right| \ln \frac{T_c}{T}. \end{aligned} \quad (31)$$

Substitution into (23) gives the field H_c . As $T \rightarrow 0$ the sum in (31) can be replaced by an integral and we get

$$A = \alpha \left| \frac{J}{N} \right| \ln \frac{\Lambda}{g\mu H_c}. \quad (32)$$

From (23) we have

$$2\alpha \left| \frac{J}{N} \right| \ln \frac{\Lambda}{g\mu H_c} = \left[1 + \alpha \left| \frac{J}{N} \right| \ln \frac{T_c}{T} \right]^{-1}.$$

Then, as $T \rightarrow 0$, the quantity $g\mu H_c \rightarrow \Lambda$ as follows

$$g\mu H_c \approx \Lambda \left[1 - \left(2\alpha \left| \frac{J}{N} \right| \ln \frac{T_c}{T} \right)^{-1} \right]. \quad (33)$$

When, on the other hand, $T \rightarrow T_c$, clearly $H_c \rightarrow 0$. Then

$$\begin{aligned} A &= B - 2\pi\alpha \left| \frac{J}{N} \right| (g\mu H_c)^2 T_c \sum_{\omega} \frac{1}{\omega^3} \\ &= B - 2\alpha \left| \frac{J}{N} \right| \frac{7}{8} \zeta(3) \left(\frac{g\mu H_c}{\pi T_c} \right)^2. \end{aligned}$$

Substituting this into (23) we find

$$g\mu H_c \approx \pi^{[6/7]\zeta(3)} T_c (T_c - T)^{1/2}. \quad (34)$$

Hence, the $H_c(T)$ curve does not at all resemble the curve of the critical field of a superconductor.

We now find the thermodynamic potential. We put $H = 0$. Taking the derivative with respect to the interaction constant, we have

$$\frac{\partial \Omega}{\partial (J/N)} = \frac{\langle \mathcal{H}_{int} \rangle}{(J/N)QV}. \quad (35)$$

The normalization $1/Q$ gives the change from the complete to the physical average. The potential Ω is normalized to unit volume.

If (in (10)) we take only $\mathcal{H}_{int,1}$ into account, we get from (35)

$$\begin{aligned} \frac{\partial \Omega}{\partial (J/N)} &= \frac{N_i}{Q} T \sum_{\omega_1} F_{\alpha\beta}^{(2)}(0, 0, \omega_1) \cdot T \sum_{\omega_2} F_{\alpha\beta}^{(4)}(0, 0, \omega_2) \sigma_{\alpha\alpha}^i \sigma_{\beta\beta}^i, \\ &- \frac{N_i}{Q} T \sum_{\omega_1} F_{\alpha\beta}^{(3)}(0, 0, \omega_1) \cdot T \sum_{\omega_2} F_{\alpha\beta}^{(4)}(0, 0, \omega_2) \sigma_{\alpha, \alpha\beta}^i \sigma_{\beta\beta}^i. \end{aligned} \quad (36)$$

Using the definition of $\Delta_{\alpha\beta}^{(i)}$, Eq. (19) for $F^{(2)}$ and a similar formula for $F^{(3)}$ we find

$$\frac{\partial \Omega}{\partial |J/N|} = -\frac{32\pi\alpha N_i}{3} \frac{1}{|J/N|} \sum_{\omega>0} \frac{\delta_0^2 + \delta_1^2}{\omega + R} = -\frac{4\delta_1^2 N_i}{|J/N|^2} = -\frac{4RN_i}{3\pi\alpha |J/N|^2}. \quad (37)$$

We have used here Eq. (24), the value $Q = 3/4$ (see Appendix), and the relation $\delta_0 = -\delta_1/\sqrt{2}$.

We write Eq. (24) in the form

$$2\alpha |J/N| f_T(R) = 1. \quad (38)$$

From (37) and (38) we have

$$\Omega - \Omega_0 = \int_0^{J/N} d \left(\frac{1}{|J/N|} \right) \frac{4RN_i}{3\pi\alpha} = \frac{8N_i}{3\pi} \int_0^R \frac{\partial f_T(R_1)}{\partial R_1} R_1 dR_1, \quad (39)$$

where Ω_0 is the value of Ω for $J = 0$. This formula can be appreciably simplified if we change from Ω to the energy $E = \Omega - T\partial\Omega/\partial T$. For this purpose we write (24) symbolically in the form

$$\frac{1}{2\alpha |J/N|} = \ln \frac{2\gamma\Lambda}{\pi T} + \sum_{n=1}^{\infty} a_n \left(\frac{R}{T} \right)^n. \quad (40)$$

Substituting into (39) we find that $\Omega - \Omega_0$ has the form

$$\Omega - \Omega_0 = \frac{8N_i}{3\pi} \sum_{n=1}^{\infty} \frac{n}{n+1} \frac{a_n R^{n+1}}{T^n}.$$

Hence we get

$$E - E_0 = -\frac{8N_i}{3\pi} T^2 \frac{\partial}{\partial T} \left(\frac{R}{T} \right) \sum_{n=1}^{\infty} n a_n \left(\frac{R}{T} \right)^n.$$

Differentiating (40) with respect to the temperature we find

$$E - E_0 = -(8N_i/3\pi)R. \quad (41)$$

Nagaoka^[3] found a similar formula, but with a coefficient $2/\pi$ instead of $8/3\pi$.

Using Eqs. (29) and (30) we can get the asymptotic values of Ω :

$$\frac{\Omega - \Omega_0}{N_i} \approx \begin{cases} -\frac{8}{3\pi} R(0) - \frac{4\pi T^2}{9R(0)} - \frac{\pi^3 T^4}{15R^3(0)}, & T \ll T_c, \\ -0.54 \frac{(T_c - T)^2}{T_c} - 0.12 \frac{(T_c - T)^3}{T_c^2}, & T_c - T \ll T_c. \end{cases} \quad (42)$$

From (41) or (42) we can find the asymptotic values of the specific heat:

$$C - C_0 = N_i \left[3.16 \frac{T}{T_c} - 36 \left(\frac{T}{T_c} \right)^3 \right], \quad T \ll T_c,$$

$$C - C_0 = N_i \left[1.08 + 0.34 \frac{T - T_c}{T_c} \right], \quad T_c - T \ll T_c. \quad (43)$$

The specific heat has thus for $T \ll T_c$ a correction proportional to N_i and linear in the temperature. As to order of magnitude, $(C - C_0)/C_0 \sim c\epsilon_F/T_c$ where c is the atomic concentration. Because of the factor ϵ_F/T_c this quantity may turn out to be large. In the vicinity of T_c we get a jump in the specific heat. In actual fact, the expressions obtained are apparently inapplicable in the immediate vicinity of T_c (see below).

To conclude this section we must dwell upon the limits of applicability of the expressions obtained. The

limitation will first of all be connected with the fact that we took in our calculations only the "pole" part of the interaction Hamiltonian $\mathcal{H}_{\text{int},1}$ into account. The problem arises of the role of $\mathcal{H}_{\text{int},2}$. This part has the same form as when there is no pairing but, drawing the diagrams, it is necessary to fit in this time not only the functions G and \mathcal{G} , but also the functions F and \mathcal{F} and after this it is necessary to subtract the "normal" expression. We shall not go into this estimate in detail. It turns out that the contribution of these terms is of order $(\alpha J/N)^2 \sim (J/\epsilon_F)^2$ as compared to the terms evaluated.

The vicinity of T_c occupies a special position. An estimate of the region in which we can expect trouble can be obtained from the following considerations. According to section 1 of the present paper, corrections from taking into account diagrams which do not occur in the chain correspond to a relative change in the interaction constant $\alpha J/N$ by the amount

$$\delta\left(\frac{J}{N}\right) \left| \left(\frac{J}{N}\right) \sim \left(\frac{J}{\epsilon_F}\right) \right.$$

This correction may compete with $|T_c - T|$ in the form (6). On this ground, the criterion for the applicability of the theory is thus of the form

$$\left| \frac{T_c - T}{T_c} \right| \gg \left(\frac{J}{\epsilon_F} \right). \quad (44)$$

4. MAGNETIC PROPERTIES

The results obtained make it possible to determine the magnetic moment of the system in any field. Expressed in terms of Green functions, the moment has the form

$$\langle M_H \rangle = M_e + M_i = \mu T \sum_{\omega, \sigma_z} G(\omega, \mathbf{r}, \mathbf{r}) \sigma_z + \frac{N_i}{Q} g \mu T \sum_{\omega, M} \mathcal{G}_{MM}(\omega) M. \quad (45)$$

One checks easily, using Eq. (16), that the first term gives simply the Pauli paramagnetism. To see this we subtract the analogous expression with $G^{(0)}$. The remainder can immediately be integrated over ξ and this gives zero. We are interested in the second term and we shall consider it now.

Taking $\mathcal{H}_{\text{int},1}$ into account, we get

$$\mathcal{G}_{\beta\beta'} = \mathcal{G}_{\beta\beta'}^{(0)} + \mathcal{G}_{\beta\beta'}^{(1)} \Delta_{\alpha\beta} F_{\alpha\beta'}^{(2)} - \Delta_{\alpha\beta} F_{\alpha\beta'}^{(3)}. \quad (46)$$

Substituting (19) and a similar expression for $F^{(3)}$ and using (13) we get

$$\begin{aligned} \mathcal{G}_{11} &= \frac{1}{i\omega + g\mu H} \left(1 + 2\pi i \alpha \text{sign } \omega \frac{\delta_0^2}{i\omega} \right) \\ &\times \left[1 + 2\pi i \alpha \text{sign } \omega \left(\frac{\delta_0^2}{i\omega} + \frac{\delta_1^2}{i\omega + \mu g H} \right) \right]^{-1}, \\ \mathcal{G}_{-1-1}(H) &= \mathcal{G}_{11}(-H), \\ \mathcal{G}_{\infty} &= \frac{1}{i\omega} + \frac{2\pi i \alpha \delta_0^2}{\omega^2} \left\{ \left[1 + 2\pi i \alpha \text{sign } \omega \left(\frac{\delta_0^2}{i\omega} + \frac{\delta_1^2}{i\omega + \mu g H} \right) \right]^{-1} \right. \\ &\left. + \left[1 + 2\pi i \alpha \text{sign } \omega \left(\frac{\delta_0^2}{i\omega} + \frac{\delta_1^2}{i\omega - \mu g H} \right) \right]^{-1} \right\}. \end{aligned} \quad (47)$$

Substituting (45) we get

$$\begin{aligned} M_i &= -\frac{2ig\mu N_i}{Q} T \sum_{\omega>0} (\omega + 2\pi\alpha\delta_0^2) \{ [\omega(\omega - ig\mu H) \\ &+ 2\pi\alpha\delta_0^2(\omega - ig\mu H) + 2\pi\alpha\delta_1^2\omega]^{-1} - [\omega(\omega + ig\mu H) \\ &+ 2\pi\alpha\delta_0^2(\omega + ig\mu H) + 2\pi\alpha\delta_1^2\omega]^{-1} \}. \end{aligned} \quad (48)$$

Bearing in mind that Q also depends on H it is clear that this is a very complicated expression. We consider limiting cases.

In the case $T = 0$ we can in Eq. (18) replace the sum by an integral

$$T \sum_{\omega} \rightarrow \frac{1}{2\pi} \int d\omega.$$

If $\mu H \ll \pi\alpha\delta^2$, the corrections to δ are of order $(\mu g H / \pi\alpha\delta^2)^2$ and can be neglected, i.e., the values of δ_0^2 and δ_1^2 are taken for $H = 0$. It is not possible to expand immediately in terms of H in (48) as the expressions inside the square brackets have a pole at the points $\omega \sim i\mu g H$ and the path around these poles gives the main contribution to the moment. Integrating and limiting ourselves all the time to terms of zeroth and first order and also taking into account that for this case $Q = 2/3$ (see the Appendix), we get

$$M_i = \frac{3}{7} N_i g \mu + \frac{8N_i(g\mu)^2 H}{21\pi^2 \alpha \delta_1^2} \left(\ln \frac{9\pi\alpha\delta_1^2}{g\mu H} + \frac{1}{2} \right). \quad (49)$$

The other interesting limiting case is that of a weak field $g\mu H \ll T$. We can then expand in (48) in terms of $g\mu H$ and we can again take for δ its value for zero field. The normalization is in that case always equal to $3/4$. Hence we get

$$M_i = \frac{16N_i(g\mu)^2 H}{3} T \sum_{\omega>0} \frac{(\omega + \pi\alpha\delta_1^2)^2}{\omega^2(\omega + 3\pi\alpha\delta_1^2)^2}. \quad (50)$$

As $T \rightarrow T_c$ the quantity $\delta_1 \rightarrow 0$ and we get

$$M_i = \frac{2}{3} \frac{N_i(g\mu)^2 H}{T}. \quad (51)$$

As $T \rightarrow 0$ we must note that the summation in (48) goes over $\omega \sim T$. We can thus assume that $\omega \ll \pi\alpha\delta_1^2$. We get then

$$M_i = \frac{2}{27} \frac{N_i(g\mu)^2 H}{T}. \quad (52)$$

It is interesting that when bound complexes are formed the Curie law is retained although the coefficient turns out to be nine times less. Such a conclusion was qualitatively obtained in [6].

Nagaoka [3] also obtained a Curie law at low temperature but with an incorrect coefficient ($1/2$ instead of $2/27$ for $S = 1$). We must also note that at $T = T_c$ the moment smoothly reaches its normal value without any correction whatever to the Kondo effect. Using the technique discussed here one can check that above the critical temperature the moment is expressed by Eq. (51) with small corrections of order J/ϵ_F .

It is very complicated to find the complete temperature dependence of the magnetic susceptibility in explicit form. However, one can obtain an interpolation formula. Using the fact that the main role in (50) is in all cases played by $\omega \approx \pi T$ we replace in the brackets in the sum ω by πT . As a result we get

$$\chi_i = \frac{M_i}{H} = \frac{2N_i(g\mu)^2}{3T} \left(\frac{\pi T + R/3}{\pi T + R} \right)^2. \quad (53)$$

Knowing the function $R(T)$, we can find $\chi(T)$.

We must, however, bear in mind that we have here considered only the case $S = 1$ and that for other cases the situation may be different. We must bear this in mind when we speak about comparing the results with experimental data.

5. THE PROBLEM OF THE ELECTRICAL RESISTIVITY

Nagaoka^[2] found an expression for the electrical resistivity at low temperatures. A similar expression can also be obtained using the Green function (16). However, all the same, the expression obtained in^[2] gives, apparently, only qualitatively the behavior of the resistivity. The point is that it is obtained without taking into account the "non-pole" part $\mathcal{H}_{int,2}$ of the interaction which in this case plays an essential role. This is clear from the fact that the "pole" part of the scattering probability $\text{Im } N_1 V^R(\omega)$, where V^R is the retarded analogue of (15), vanishes at $T = T_C$ while the part connected with $\mathcal{H}_{int,2}$ has clearly the same order of magnitude as $\text{Im } N_1 V^R(\omega)$ for $T = 0$.

The complete temperature dependence of the resistivity can be described as follows. Above T_C the resistivity ρ increases because of the Kondo effect when the temperature decreases and is expressed by the formula obtained in^[7]. In the vicinity of T_C this formula no longer applies as the difference $1 - 2|J/N| \alpha \ln(\Lambda/T_C)$ which occurs in the denominator is of order $|J/N| \alpha$ and the next orders of magnitude must be taken into account.

As to order of magnitude $\rho(T_C)$ must be the same as for resonance scattering, i.e., $\rho \sim cm/\alpha e^2 \sim c/e^2 p_0$, where c is the atomic concentration of the impurity. When the temperature is lowered the lower limit of the logarithmic integrals must remain of order T_C as the temperature cut-off is replaced by a cut-off because of the appearance of δ . On the other hand, in this region the pole part appears which not too close to T_C is of the same order of magnitude. The temperature dependence of the non-pole part of the resistivity will for $T \ll T_C$ be connected primarily with the change in δ , i.e., it will have the relative order $(T/\pi\alpha\delta^2)^2$. The temperature correction from the pole part has the same form. Hence it follows that for $T \ll T_C$

$$\rho = \rho(0) [1 - q(T/T_C)^2], \tag{54}$$

where $\rho(0) \sim cm/\alpha e^2$, $q \sim 1$. This formula is very similar to the one obtained when there is only one, "pole," part but, of course, the numerical values of the coefficients must be different. This fact must be borne in mind when comparison is made with experiments.²⁾

Unfortunately, the advantages enjoyed by the case $S = 1$ does not at all manifest itself in calculating the resistivity as in the non-pole part states with total spin $S = 1/2$ take part and for those the "parquet" equation remains.

The most important result of the present paper is the fact that in any case for $S = 1$ bound states indeed and are energetically advantageous. For other values of the spin this has, of course, not been shown rigorously, but it is very probable.

²⁾Preliminary estimates show that the non-pole part for $T \ll T_C$ is at most of order of magnitude $(T/T_C)^2$. Because of this $\rho(0)$ is for $T = 0$ given by only the pole part. From (15), (16), and (14) we get $\rho(0) = 16\pi c/3(z e^2 p_0)$, where z is the number of electrons per atom of the basic metal. (Added in proof, November 14, 1967).

On the other hand, in the work of Suhl and Wong^[7] and Maleev^[8], who start from the absence of a bound state, the case $S = 1$ is not at all a special one. One can conclude from this that the scattering amplitude without singularities corresponding to the absence of a bound state can be obtained even in the case where it surely can exist. From energetic considerations one must prefer a bound state.

The experimental data on the temperature dependence of the resistivity also favor this. Although both theories predict at $T = 0$ an approach to a finite value of the same order of magnitude, in the case of bound states this approach follows Eq. (54) while if they are absent the temperature correction is of order $1/\ln^2(\Lambda/T)$. Daybell and Steyert's experiments^[6] agree well with Eq. (54).

APPENDIX

We evaluate the magnitude of the normalization Q when there are bound states. From Eq. (3), the footnote referring to it and the definition (8) we have

$$Q = 1/2 \langle \delta^2 \rangle = 1/2 \langle \hat{N}(3 - \hat{N}) \rangle = \frac{3}{2} T \sum_{\omega} \mathcal{G}_{\beta\beta}(\omega) e^{i\omega\tau} - \frac{1}{2} \left[T \sum_{\omega} \mathcal{G}_{\beta\beta}(\omega) e^{i\omega\tau} \right]^2 + \frac{1}{2} T^2 \sum_{\omega_1} \mathcal{G}_{\beta\beta,(\omega_1)} e^{-i\omega_1\tau} \sum_{\omega_2} \mathcal{G}_{\beta,\beta}(\omega_2) e^{i\omega_2\tau} - \frac{1}{2} T^2 \sum_{\omega_1} \mathcal{D}_{\beta\beta,(\omega_1)}^+ \sum_{\omega_2} \mathcal{D}_{\beta\beta,(\omega_2)}, \tag{A1}$$

where $\tau \rightarrow +0$.

We found the function \mathcal{G} earlier. Similarly we can determine also the functions \mathcal{D} and \mathcal{D}^+ . To do this it is necessary to express them in terms of the $F^{(i)}$ as was done in section 4 for \mathcal{G} and then to use Eq. (19) for $F^{(2)}$ and similar formulae for the other $F^{(i)}$. It turns out that all the $\mathcal{D}_{\beta\beta}$ vanish. When substituting into (A1) we take into account the rule for taking sums with factors $e^{i\omega\tau}$ (see^[4]):

$$T \sum_{\omega} \mathcal{G}(\omega) e^{i\omega\tau} = 2T \sum_{\omega > 0} \text{Re } \mathcal{G}(\omega) + 1/2 \text{sign } \tau.$$

As a result (see (47)) we get (when $g\mu H \ll \pi\alpha\delta^2$)

$$T \sum_{\omega} \mathcal{G}_{MM}(\omega) e^{i\omega\tau} = 2T \sum_{\omega > 0} \frac{\mu g H M}{\omega^2 + (\mu g H M)^2} \frac{\omega + \pi\alpha\delta_1^2}{\omega + 3\pi\alpha\delta_1^2} + \frac{1}{2} \text{sign } \tau = \frac{1}{2} \left(\frac{1}{3} \text{th } \frac{\mu g H M}{2T} + \text{sign } \tau \right),$$

since only $\omega \sim \mu g H$ or $\omega \sim T$ are important.

Substituting these results into (A1) we get

$$Q = \frac{3}{4} + \frac{1}{36} \text{th}^2 \frac{\mu g H}{2T} \tag{A2}$$

When $\mu g H \ll T$, we have $Q = 3/4$ and also for $\delta = 0$, while when $\mu g H \gg T$ we shall have $Q = 7/9$. It thus turns out that for $H = 0$ the quantity $Q = 3/4$ for all temperatures. In the vicinity of the critical temperature ($\pi\alpha\delta^2 \ll T$) we can use Eq. (5).

There remains the limiting case $\mu g H \gg T$, $\pi\alpha\delta^2$. It is clear that then δ is not at all important and $Q = 1$. The expression for Q is more complicated in the intermediate regions, in particular when $\mu g H \sim \pi\alpha\delta^2 \gtrsim N$. However, in that case most interest centers around the critical field and this is evaluated without normalization (see Sec. 3).

¹A. A. Abrikosov, Zh. Eksp. Teor. Fiz. **53**, 1078 (1967) [Sov. Phys.-JETP **26**, 641 (1968)].

²Y. Nagaoka, Phys. Rev. **138**, A1112 (1965).

³Y. Nagaoka, Progr. Theor. Phys. **37**, 13 (1967).

⁴A. A. Abrikosov, L. P. Gor'kov, and I. E. Dzyaloshinskiĭ, *Metody kvantovoi teorii polya v statisticheskoi fizike* (Quantum Field Theory Methods in Statistical Physics) Fizmatgiz, 1962 [English translation published by Pergamon Press, 1965].

⁵A. A. Abrikosov, Physics, **2**, 5 (1965).

⁶M. D. Daybell and W. A. Steyert, Phys. Rev. Lett. **18**, 398 (1967).

⁷H. Suhl and D. Wong, Physics **3**, 17 (1967).

⁸S. V. Maleev, Zh. Eksp. Teor. Fiz. **51**, 1940 (1966); **53**, 1038 (1967) [Sov. Phys.-JETP **24**, 1300 (1967); **26**, 620 (1968)].

Translated by D. ter Haar
239