

## Correlation Effects and Superconductivity in Dilute Alloys with Localized States

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We study the effect of transitional impurities on the superconducting critical temperature of normal metals: we restrict our considerations to the impurities which give rise to virtual bound states (localized states) but do not have magnetic moments. We use Gor'kov's method to study the superconducting state and Anderson's Hamiltonian to describe the impurity effect. The virtual bound state gives two contributions to the decrease of the critical temperature. The first one, pointed out by Zuckermann, is due to the resonance scattering only, and hence depends on the relaxation time of the conduction electrons; the second one, which is studied here in detail, is produced by the Coulomb interaction within the localized states. In fact, because of the admixture of localized and conduction states, a part of this Coulomb repulsion appears in the interaction of conduction states and then changes the binding energy of a pair. It is shown that our problem is connected with the study of Schrieffer and Mattis on correlation effects; in particular, we find that the same effective Coulomb interaction determines the properties of the system. Finally, we compare our formulas with the experimental results for Al- and Zn-base alloys. A reasonable agreement is found.

### I. INTRODUCTION

IMPURITIES have different effects on the properties of a metal in its superconducting state, depending on the nature of the impurities themselves.

The two extreme cases are:

(1) magnetic impurities which rapidly destroy superconductivity because of the exchange interaction between the conduction electrons and the magnetic impurity atoms;

(2) non-transition-metal impurities which have only a small effect on the critical temperature, due to the destruction of the anisotropy of the gap.

An intermediary case occurs with alloys containing transitional impurities which do not have magnetic moments. It has been suggested by Boato *et al.*<sup>1</sup> that this effect is due to the existence of a virtual bound state (or localized state)<sup>2</sup> on each impurity. Zuckermann<sup>3</sup> has calculated the influence of the resonance scattering, caused by such impurities, on the transition of the alloy to the superconducting state. Although this calculation is correct and gives an appreciable change in the critical temperature, using this model one has to assume, nevertheless, small widths for the localized states, in order to explain the experimental results.

In this paper, we want to demonstrate that the

Coulomb interaction between the  $d$  states plays a crucial role in decreasing the critical temperature. In fact, because of the admixture between localized and conduction electrons, a part of this repulsion is present in the interaction of the two electrons of a pair. To understand this, let us remember that we can build up a Bardeen-Cooper-Schrieffer (BCS) wave function coupling the one-electron state

$$\phi_n = \sum_k \langle n | k \rangle \phi_k + \langle n | d \rangle \phi_d$$

eigenfunction of the one-body part of the Hamiltonian, with its time-reversed correspondent

$$\phi_{-n} = (\phi_n)^* = \sum_k \langle n | k \rangle^* \phi_{-k} + \langle n | d \rangle^* \phi_{-d},$$

which is also an eigenstate of the one-electron Hamiltonian. Here,  $\phi_k$  and  $\phi_d$  are, respectively, the Bloch functions for the conduction band in the pure metal and the unperturbed localized  $d$  state; we use the shorthand notation  $k \equiv (k, \uparrow)$ ,  $-k \equiv (-k, \downarrow)$ ,  $d \equiv (d, \uparrow)$ ,  $-d \equiv (d, \downarrow)$ . The matrix elements of the two-body interaction between these new states are decreased because of the presence of the Coulomb repulsion, i.e., because of the admixture of the localized orbitals with the conduction states.

Let us say a few words about the approach which is used in treating the virtual bound state. In superconductivity problems, one studies the motion of an electron pair in the average field of all other pairs; for our problem, this means that we take into account in the averaging process such terms as

$$U \langle a_d^\dagger a_{-d}^\dagger \rangle.$$

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<sup>1</sup> G. Boato, G. Gallinaro, and C. Rizzuto, *Phys. Letters* **5**, 20 (1963).

<sup>2</sup> P. W. Anderson, *Phys. Rev.* **124**, 41 (1961). For a detailed analysis of the concept of localized state and of the experimental situation see J. Friedel, *J. Phys. Radium* **23**, 692 (1962).

<sup>3</sup> M. J. Zuckermann, *Phys. Rev.* **140**, A889 (1965).

Thus, the impurity is treated outside the one-electron theory (usual Hartree-Fock approximation), and the correlation between  $d$  electrons is partly described.

Recently, many papers have appeared studying the correlation between  $d$  electrons in a  $d$  band or on an impurity atom, mainly to discuss the conditions under which the atom can have a magnetic moment. It is evident that our results should be connected *a priori* with their conclusions. In fact, we find that the change in the critical temperature depends not on the Coulomb potential  $U$  itself, because of the admixture of conduction and localized electrons, but on an effective potential  $U_{\text{eff}}$ . This is the same effective potential found by Schrieffer and Mattis in their paper on the effect of correlation on localized states.<sup>4</sup>

In Sec. II, we discuss the method of approach which is an application of Gor'kov's method<sup>5</sup> to Anderson's Hamiltonian<sup>2</sup> (without orbital degeneracy). The problem with one impurity is discussed in Sec. III.

In Sec. IV, an expression for the critical temperature  $T_c$  of an isotropic dilute alloy is derived, and the approximations made in calculating this result are discussed. It is found that the decrease in  $T_c$  can be decomposed into two parts: the first one, due to the resonance scattering, depends on the relaxation time of the conduction electrons (Zuckermann's result); the second one is due to the Coulomb repulsion between the electrons when they are in the localized states.

In Sec. V, we compare our formula with experimental results for Al and Zn alloys by Boato, Gallinaro, and Rizzuto,<sup>6</sup> and by Aoki and Ohtsuka,<sup>7</sup> obtaining a good order of magnitude agreement for parameters describing the resonant state.

In the Appendix, we generalize our results to the case of orbitally degenerate states.

## II. THE HAMILTONIAN AND THE METHOD

For the sake of simplicity, we begin by studying a single transition-metal atom imbedded in a nontransition metal in its superconducting state; here we limit our considerations to the case of an impurity which has a single nondegenerate " $d$ " level. Later, we shall treat the problem of dilute alloys (Sec. IV) and extend the calculations to the case of an orbitally degenerate  $d$  level (Appendix).

We shall study this problem using Anderson's Hamiltonian,<sup>2</sup> to which we have added the BCS interaction among conduction electrons:

$$H = H_0 + H_1 + H_2,$$

where, in second-quantized notation,

$$\begin{aligned} H_0 &= \sum_k \epsilon_k n_k + \sum_d \epsilon_d n_d, \\ H_1 &= \sum_{k,d} (V_{dk} a_d^\dagger a_k + V_{kd} a_k^\dagger a_d), \\ H_2 &= U n_d n_{-d} + \frac{1}{2} \sum_{kk'} \lambda_{kk'} a_k^\dagger a_{-k}^\dagger a_{-k'} a_{k'}. \end{aligned} \quad (1)$$

Here,  $\epsilon_k$  and  $\epsilon_d$  are the energies of the Bloch states in the conduction band of the pure metal and of the unperturbed localized  $d$  state, respectively. The energies are measured from the Fermi level. As usual, we assume that the matrix elements  $\lambda_{kk'}$  of the superconducting interaction have nonvanishing values only when both  $|\epsilon_k|$  and  $|\epsilon_{k'}|$  are less than the Debye frequency  $\omega_D$  of the pure metal.

We neglect the one-body terms which describe the nonresonance scattering of conduction electrons,

$$H_1' = \sum_{k,k'} V_{kk'} a_k^\dagger a_{k'},$$

since their effect should be small in comparison with the effect due to the resonance scattering.<sup>3</sup>

We start by writing down the equations of motion for the various unperturbed creation operators:

$$\begin{aligned} [H, a_k^\dagger] &= \epsilon_k a_k^\dagger + V_{dk} a_d^\dagger + \sum_{k'} \lambda_{kk'} a_{k'}^\dagger a_{-k'}^\dagger a_{-k}, \\ [H, a_d^\dagger] &= \epsilon_d a_d^\dagger + \sum_k V_{kd} a_k^\dagger + U a_d^\dagger a_{-d}^\dagger a_{-d}. \end{aligned} \quad (2)$$

We linearize these equations, obtaining the usual Hartree-Fock terms, and terms which take into account the condensation in pairs of the one-electron states, i.e.,

$$\begin{aligned} [H, a_k^\dagger] &= \epsilon_k a_k^\dagger + V_{dk} a_d^\dagger + \sum_{k'} \lambda_{kk'} \langle a_{k'}^\dagger a_{-k'}^\dagger \rangle a_{-k}, \\ [H, a_d^\dagger] &= E a_d^\dagger + \sum_k V_{kd} a_k^\dagger + U \langle a_d^\dagger a_{-d}^\dagger \rangle a_{-d}, \end{aligned} \quad (3)$$

where

$$E = \epsilon_d + \langle n \rangle U,$$

with  $\langle n \rangle \equiv \langle n_d \rangle = \langle n_{-d} \rangle$  the average number of the  $d$  (and  $-d$ ) electrons. In the first equation, we have not written explicitly the other terms arising by the linearization, since they lead only to a correction in the one-electron energies.

The expectation values  $\langle a_k^\dagger a_{-k}^\dagger \rangle$  and  $\langle a_d^\dagger a_{-d}^\dagger \rangle$  are taken between the condensed states  $\psi_N$  and  $\psi_{N+2}$ , with  $N$  and  $N+2$  electrons, respectively. Later, we shall demonstrate, by means of self-consistent equations, that the term  $\langle a_d^\dagger a_{-d}^\dagger \rangle$  is indeed nonvanishing; it means that the number of  $d$  electrons may fluctuate, since the number of electrons in the condensed state may fluctuate. In this way, some aspects of the correlation between  $d$  electrons are treated in a simple manner.

In the equations of motion, we do not have, explicitly,

<sup>4</sup> J. R. Schrieffer and D. C. Mattis, Phys. Rev. **140**, A1412 (1965).

<sup>5</sup> L. P. Gor'kov, Zh. Eksperim. i Teor. Fiz. **36**, 1918 (1959) [English transl.: Soviet Phys.—JETP **2**, 1364 (1959)].

<sup>6</sup> G. Boato, G. Gallinaro, and C. Rizzuto, Phys. Rev. Letters **5**, 20 (1963); Rev. Mod. Phys. **36**, 162 (1964); Phys. Rev. **148**, 353 (1966).

<sup>7</sup> A. Aoki and T. Ohtsuka, Phys. Letters **19**, 456 (1965).

terms like  $\langle a_k^\dagger a_{-d}^\dagger \rangle$ , since our Hamiltonian has no two-body interactions mixing free and  $d$  states.

Let us go on with Gor'kov's method.<sup>5,8</sup> Since we shall study physical properties of our system at finite temperature later, we use thermodynamic Green's functions.

Let us define

$$\begin{aligned} G(k, k'; t) &= -\langle T[a_k(t)a_{k'}^\dagger(0)] \rangle, \\ F^\dagger(k, k'; t) &= \langle T[a_{-k}^\dagger(t)a_{k'}^\dagger(0)] \rangle, \\ G(k, d; t) &= -\langle T[a_k(t)a_d^\dagger(0)] \rangle, \\ F^\dagger(k, d; t) &= \langle T[a_{-k}^\dagger(t)a_d^\dagger(0)] \rangle, \end{aligned}$$

and so on, where  $\langle \dots \rangle$  is the statistical average for a grand canonical ensemble and  $T$  is Dyson's time-ordering operator; the operators  $a(t)$  and  $a^\dagger(t)$  are in a Heisenberg-like representation.

Equations for the  $G$  and  $F^\dagger$  functions can be obtained from Eqs. (3), since  $dA/dt = [H, A]$ . Finally, taking the Fourier components of these equations, one obtains Gor'kov's equations:

$$(i\omega - \tilde{H})G_\omega + \Delta F_\omega^\dagger = 1, \quad (4a)$$

$$(i\omega + \tilde{H})F_\omega^\dagger + \Delta^* G_\omega = 0, \quad (5a)$$

where  $\Delta$  is the "gap function" and  $\tilde{H}$  the Hartree-Fock Hamiltonian for the normal metal. The frequency  $\omega$  has only discrete values, i.e.,

$$\omega = \omega_n \equiv (2n+1)\pi T,$$

where  $n$  is an integer and  $T$  the temperature of the system. The Fourier components are defined as

$$G(k, k'; t) = T \sum_{\omega} e^{-i\omega t} G_\omega(k, k'),$$

and so on, for the other functions.

For our case, the Hartree-Fock Hamiltonian is

$$\tilde{H} = \sum_k \epsilon_k n_k + E \sum_d n_d + \sum_{k,d} (V_{dk} a_d^\dagger a_k + V_{kd} a_k^\dagger a_d), \quad (6)$$

and the matrix elements of the "gap" are

$$\begin{aligned} \Delta_k &\equiv -\sum_{k'} \lambda_{kk'} \langle a_{k'} a_{-k'} \rangle, \\ \Delta d &\equiv -U \langle a_d a_{-d} \rangle, \\ \Delta_k^* &\equiv -\sum_{k'} \lambda_{k'k} \langle a_{-k'}^\dagger a_{k'}^\dagger \rangle, \\ \Delta_d^* &\equiv -U \langle a_{-d}^\dagger a_d^\dagger \rangle. \end{aligned}$$

Then, Eqs. (4a) and (5a) can be written

$$\begin{aligned} (i\omega - \epsilon_k)G_\omega(k, k') - V_{kd}G_\omega(d, k') \\ + \Delta_k F_\omega^\dagger(k, k') = \delta_{kk'}, \end{aligned}$$

$$\begin{aligned} (i\omega - \epsilon_k)G_\omega(k, d) - V_{kd}G_\omega(d, d) \\ + \Delta_k F_\omega^\dagger(k, d) = 0, \end{aligned} \quad (4b)$$

$$\begin{aligned} (i\omega - E)G_\omega(d, k) - \sum_{k'} V_{dk'}G_\omega(k', k) \\ + \Delta_d F_\omega^\dagger(d, k) = 0, \end{aligned}$$

$$\begin{aligned} (i\omega - E)G_\omega(d, d) - \sum_k V_{dk}G_\omega(k, d) \\ + \Delta_d F_\omega^\dagger(d, d) = 1; \end{aligned}$$

$$\begin{aligned} (i\omega + \epsilon_k)F_\omega^\dagger(k, k') + V_{kd}F_\omega^\dagger(d, k') \\ + \Delta_k^* G_\omega(k, k') = 0, \end{aligned}$$

$$\begin{aligned} (i\omega + \epsilon_k)F_\omega^\dagger(k, d) + V_{kd}F_\omega^\dagger(d, d) \\ + \Delta_k^* G_\omega(k, d) = 0, \end{aligned} \quad (5b)$$

$$\begin{aligned} (i\omega + E)F_\omega^\dagger(d, k) + \sum_{k'} V_{dk'}F_\omega^\dagger(k', k) \\ + \Delta_d^* G_\omega(d, k) = 0, \end{aligned}$$

$$\begin{aligned} (i\omega + E)F_\omega^\dagger(d, d) + \sum_k V_{dk}F_\omega^\dagger(k, d) \\ + \Delta_d^* G_\omega(d, d) = 0. \end{aligned}$$

We want to point out that  $|\Delta_d|^2$  does not have the usual meaning of energy needed for breaking a pair, but, as we have already said, that it represents the possibility for  $d$  electrons to fluctuate in number.

### III. DISCUSSION OF THE ONE IMPURITY PROBLEM

The Green's functions  $\tilde{G}$  for the electrons in the normal metal satisfy, in the Hartree-Fock approximation, Eqs. (4) with vanishing  $F^\dagger$  (and  $\Delta$ ):

$$(i\omega - \tilde{H})\tilde{G}_\omega = 1. \quad (7)$$

These equations are given by Anderson.<sup>2</sup> We have also, for  $\tilde{G}_{-\omega}$ :

$$\begin{aligned} (-i\omega - \epsilon_k)\tilde{G}_{-\omega}(-k', -k) \\ - V_{kd}\tilde{G}_{-\omega}(-k', -d) = \delta_{k,k'}, \\ (-i\omega - \epsilon_k)\tilde{G}_{-\omega}(-d, -k) \\ - V_{kd}\tilde{G}_{-\omega}(-d, -d) = 0, \\ (-i\omega - E)\tilde{G}_{-\omega}(-k, -d) \\ - \sum_{k'} V_{dk'}\tilde{G}_{-\omega}(-k, -k') = 0, \\ (-i\omega - E)\tilde{G}_{-\omega}(-d, -d) \\ - \sum_k V_{dk}\tilde{G}_{-\omega}(-d, -k) = 1. \end{aligned} \quad (8)$$

Comparing Eqs. (4) and (5) with Eqs. (7) and (8), we find the usual integral equations

$$\begin{aligned} G &= \tilde{G}_\omega - \tilde{G}_\omega \Delta F_\omega^\dagger, \\ F_\omega^\dagger &= \tilde{G}_{-\omega} \Delta^* G. \end{aligned} \quad (9)$$

<sup>8</sup> A. A. Abrikosov, L. P. Gor'kov, and J. E. Dzyaloshinski, *Methods of Quantum Field Theory in Statistical Physics* (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1963).

These equations have, in our problem, the explicit form

$$G_{\omega}(k, k') = \tilde{G}(k, k') - \sum_{k''} \tilde{G}_{\omega}(k, k'') \Delta_{k''} F_{\omega}^{\dagger}(k'', k') - \tilde{G}_{\omega}(k, d) \Delta_d F_{\omega}^{\dagger}(d, k'),$$

$$F_{\omega}^{\dagger}(k, k') = \sum_{k''} \tilde{G}_{-\omega}(-k'', -k) \Delta_{k''}^* G_{\omega}(k'', k') + \tilde{G}_{-\omega}(-d, -k) \Delta_d^* G_{\omega}(d, k'),$$

and similarly for the other matrix elements.

Substituting the expression for  $F_{\omega}^{\dagger}(d, d)$  into the relation

$$\Delta_d^* = -UT \sum_{\omega} F_{\omega}^{\dagger}(d, d), \quad (10)$$

we get

$$\Delta_d^* = -UT \sum_{\omega} \{ \Delta_d^* \tilde{G}_{-\omega}(-d, -d) G_{\omega}(d, d) + \sum_k \Delta_k^* \tilde{G}_{-\omega}(-k, -d) G_{\omega}(k, d) \},$$

which can be written

$$\Delta_d^* = -T \sum_{\omega} \sum_k \Delta_k^* \tilde{G}_{-\omega}(-k, -d) G_{\omega}(k, d) t_d, \quad (11)$$

where  $t_d$  represents the  $t$  matrix relative to the interaction between the two  $d$  electrons and satisfies

$$t_d = U + UT \sum_{\omega} \tilde{G}_{-\omega}(-d, -d) G_{\omega}(d, d) t_d, \quad (12a)$$

where

$$\tilde{G}_{\omega}(d, d) = 1/(i\omega\chi - E),$$

$$\chi = 1 + \Gamma/|\omega|.$$

Let us limit our considerations to the case in which the half-width  $\Gamma$  of the resonance is much greater than the gap, i.e.,

$$\Gamma \gg T_c$$

(this is the case which is physically interesting). The equation for  $t_d$  at the critical temperature is then the same as in the paper of Schrieffer and Mattis<sup>4</sup>:

$$t_d(T_c) = U + U(1/2\pi) \int d\omega \tilde{G}_{-\omega}(-d, -d) \tilde{G}_{\omega}(d, d) t_d(T_c). \quad (12b)$$

The diagrammatic series described by Eq. (12b) is shown in Fig. 1. If we close one of the electron lines into itself in each diagram of the series, we find, in the low-density limit, the self-energy of the localized state, i.e., just the quantity treated by Schrieffer and Mattis.

Thus,  $t_d(T_c)$  is equal to the effective interaction of

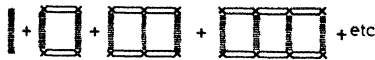


FIG. 1. Diagrammatic series for the  $t$  matrix relative to the interaction of the localized states with opposite spin. The Green's functions are those relative to the normal state.

Schrieffer and Mattis:

$$t_d(T_c) \equiv U_{\text{eff}} = \frac{U}{1 + (U/\pi E) \tan^{-1}(E/\Gamma)}. \quad (13)$$

The presence of  $t_d$  is not surprising, and, in fact, it has to appear in the set of diagrams in which two electrons multiply scatter each other. The normal state is unstable with respect to bound-pair formation and, when we arrive at this instability (from the normal state), the  $t$  matrix between the exact one-electron states ( $\phi_n$  of our Introduction) becomes singular.

Now, Eq. (11) has a clear physical meaning: the localized electron coupling ( $\Delta_d^*$ ) is induced by the condensation of the conduction electrons ( $\Delta_k^*$ ), owing to the admixture of the two kinds of states [ $\tilde{G}_{-\omega}(-k, -d) \tilde{G}_{\omega}(k, d)$ ]. It obviously depends on the effective potential between the localized electrons themselves, i.e.,  $t_d$ .

#### IV. DILUTE ALLOYS

One can calculate the transition temperature of alloys with a small concentration of impurities generalizing our Hamiltonian (1) by adding, as in Zuckermann's paper, a sum over the impurities which are taken to be randomly distributed with  $n_I$  per unit volume.

We still consider nondegenerate localized states in order to simplify our demonstration. In the Appendix we carry out the calculation relative to degenerate  $d$  orbitals.

With obvious generalizations of the definitions of  $G$  and  $F$  functions and of the "gaps"  $\Delta^*$ , we get a system of equations identical to (4) and (5) with an integral representation as in (9).

To calculate the critical temperature, we use the method developed by Abrikosov and Gor'kov.<sup>3,8,9</sup>

When the system is in its normal state (i.e., at a temperature greater than the critical temperature  $T_c$  at which the alloy becomes superconducting), these equations do not have solutions with nonvanishing  $F^{\dagger}$  (and  $\Delta$ ). At the critical temperature, we can write, retaining only the terms linear in  $F^{\dagger}$  and  $\Delta$ ,

$$G_{\omega} \simeq \tilde{G}_{\omega},$$

$$F_{\omega}^{\dagger} \simeq \tilde{G}_{-\omega} \Delta^* \tilde{G}_{\omega}.$$

Using the definition of the  $\Delta$  functions, we get immediately

$$\Delta_k^* = -T_c \sum_{\omega} \sum_{k'} \lambda_{k'k} \{ \sum_{k''} \Delta_{k''}^* \tilde{G}_{\omega}(k'', k') \tilde{G}_{-\omega}(-k'', -k') + \sum_j \Delta_j^* \tilde{G}_{\omega}(j, k') \tilde{G}_{-\omega}(-j, -k') \}, \quad (14)$$

$$\Delta_j^* = -UT_c \sum_{\omega} \sum_k \{ \sum_k \Delta_k^* \tilde{G}_{\omega}(k, j) \tilde{G}_{-\omega}(-k, -j) + \sum_i \Delta_i^* \tilde{G}_{\omega}(i, j) \tilde{G}_{-\omega}(-i, -j) \},$$

where  $j$  refers to the impurity at the site  $R_j$ .

<sup>9</sup> C. Caroli, P. G. deGennes, and J. Matricon, J. Phys. Radium 13, 707 (1962).

We must average this system over the position of the impurity atoms. As usual, we take independently the average of  $\Delta^*$  and of the product of the two Green's functions.

As long as we consider an isotropic superconductor, we can take the superconducting interaction parameter  $\lambda_{kk'}$  constant; when both  $|\epsilon_k|$  and  $|\epsilon_{k'}|$  are less than the Debye frequency  $\omega_D$ , we assume

$$\begin{aligned}\lambda_{kk'} &= \lambda, \\ \Delta_k^* &= \Delta^*.\end{aligned}$$

After these simplifications, the system (14) gives the following equation:

$$\frac{1}{|\lambda|} = T_c \sum_{\omega} \sum_{k'} \sum_k \left[ S_{\omega}(k, k') - n_I \frac{U}{1 + UT_c \sum_{\omega} \sum_j S_{\omega}(i, j)} \right. \\ \left. \times T_c \sum_{\omega'} S_{\omega'}(k, i) S_{\omega}(i, k') \right], \quad (15)$$

where  $\sum_k^D$  means summing only over momenta  $k$  with  $|\epsilon_k| < \omega_D$ . With  $S_{\omega}$ , we have indicated the average of the product of two Green's functions, i.e., for example,

$$S_{\omega}(k, k') = \langle \tilde{G}_{\omega}(k, k') \tilde{G}_{-\omega}(-k, -k') \rangle_{av}.$$

The evaluation of  $S_{\omega}(k, k')$  can be reduced, as usual, to a summation of "ladder diagrams"<sup>28</sup>

$$\begin{aligned}S_{\omega}(k, k') &= \tilde{G}_{\omega}(k) \tilde{G}_{-\omega}(-k) [\delta_{k, k'} + n_I \sum_{k''} |V_{kd}|^2 \\ &\times \tilde{G}_{\omega}(d) \tilde{G}_{-\omega}(-d) |V_{dk''}|^2 S_{\omega}(k'', k')], \quad (16)\end{aligned}$$

where  $\tilde{G}_{\omega}(k)$  and  $\tilde{G}_{\omega}(d)$  are the averaged Green's functions for electrons in the alloy in its normal state,<sup>3</sup>

$$\tilde{G}_{\omega}(k) = 1/(i\omega\eta - \epsilon_k), \quad (17a)$$

$$\tilde{G}_{\omega}(d) = 1/(i\omega\chi - E), \quad (17b)$$

with

$$\eta = 1 + \frac{n_I}{\pi g(0)} \frac{\Gamma\chi}{\omega^2\chi^2 + E^2}$$

and

$$\chi = 1 + \Gamma/|\omega|,$$

where  $g(0)$  is the density of states at the Fermi energy in the pure metal.

To simplify the solution of Eq. (15), we substitute for  $|V_{kd}|^2$  its average  $|V|^2$  over the electron momenta; summing over  $k$  we obtain  $\sum_k S_{\omega}(k, k')$  and hence

$$\begin{aligned}S_{\omega}(k, k') &= S_{\omega}(k) \left[ \delta_{k, k'} + n_I S_{\omega}(d) |V|^4 \right. \\ &\times \left. \frac{S_{\omega}(k')}{1 - n_I S_{\omega}(d) |V|^4 \sum_{k''} S_{\omega}(k'')} \right], \quad (18)\end{aligned}$$

where  $S_{\omega}(k) = \tilde{G}_{\omega}(k) \tilde{G}_{-\omega}(-k)$ , etc.

All other  $S$  functions are related to  $S_{\omega}(k, k')$ ; for instance,

$$S_{\omega}(j, k) = \sum_{k'} S_{\omega}(d) |V|^2 S_{\omega}(k', k),$$

and so on, in a similar way.

These expressions can be evaluated, remembering that

$$\sum_k^D S_{\omega}(k) = g(0) \int_{-\omega_D}^{\omega_D} \frac{d\epsilon}{\epsilon^2 + \eta^2 \omega^2} = \frac{2g(0)}{\eta|\omega|} \tan^{-1} \frac{\omega_D}{\eta|\omega|}.$$

The sum over  $\omega$  in Eq. (15) does not diverge, owing to the cut at  $\eta|\omega| \sim \omega_D$  provided by  $\tan^{-1}[\omega_D/(\eta|\omega|)]$ . Since the position of the cut is not greatly affected by the value of  $\eta$ ,<sup>9</sup> we can simply write  $\tan^{-1}(\omega_D/|\omega|)$ . When this cut is not important for the convergence of the sum, we completely neglect it (this approximation does not greatly affect the result when  $\omega_D \gg T_c$ , as it is always the case).

We are interested in the low impurity concentration range; thus, we retain in formula (15) for the critical temperature only the terms linear in the concentration, using the following expressions:

$$\begin{aligned}\sum_k^D \sum_{k'}^D S_{\omega}(k, k') &\sim \frac{2g(0)}{|\omega|} \tan^{-1} \frac{\omega_D}{|\omega|} \\ &- n_I \frac{\Gamma}{|\omega| [E^2 + (|\omega| + \Gamma)^2]} + O(n_I^2),\end{aligned}$$

$$\sum_k^D S_{\omega}(k, d) \sim \frac{\Gamma}{|\omega| [E^2 + (|\omega| + \Gamma)^2]} + O(n_I),$$

$$\sum_j S_{\omega}(i, j) \sim \frac{1}{E^2 + (|\omega| + \Gamma)^2} + O(n_I).$$

These sums can be evaluated introducing the digamma function  $\psi(z)$ :

$$\begin{aligned}A &\equiv 2 \sum_{n>0} \frac{1}{(2n+1)[(2n+1+x)^2 + y^2]} \\ &= -\frac{1}{y} \operatorname{Im} \left\{ \frac{1}{z} \left[ \psi\left(\frac{z+1}{2}\right) - \psi\left(\frac{z}{2}\right) \right] \right\},\end{aligned}$$

$$B \equiv 2 \sum_{n>0} \frac{1}{(2n+1+x)^2 + y^2} = \frac{1}{y} \operatorname{Im} \psi\left(\frac{z+1}{2}\right),$$

where  $z = x + iy$ . In our case,  $x = \Gamma/\pi T_c$  and  $y = E/\pi T_c$ .

As  $x \gg 1$ , we can use the asymptotic expressions for  $\psi$  to get

$$A \simeq \frac{1}{x^2 + y^2} \left[ \ln 2\gamma \sqrt{(x^2 + y^2)} - \frac{x}{y} \tan^{-1} \frac{y}{x} \right],$$

$$B \simeq (1/y) \tan^{-1}(y/x),$$

where  $\gamma$  is Euler's constant.

Let us come back to Eq. (15). The expression

$$2T_c \sum_{\omega} \frac{1}{|\omega|} \tan^{-1} \frac{\omega_D}{|\omega|} \sim \ln \frac{2e\gamma \omega_D}{\pi T_c}$$

appears when summing  $S_{\omega}(k, k')$  over  $\omega$ ,  $k$ , and  $k'$ ; from BCS theory, we have

$$\frac{1}{|\lambda|g(0)} = \ln \frac{2e\gamma \omega_D}{\pi T_{c0}},$$

where  $T_{c0}$  is the critical temperature of the pure metal. With the help of these relations, one immediately obtains

$$\ln \frac{T_c}{T_{c0}} \sim \frac{\Delta T_c}{T_{c0}} = -n_I \alpha \frac{g_d(0)}{g(0)} [1 + \alpha g_d(0) U_{\text{eff}}], \quad (19)$$

where

$$\alpha = \ln \left( 2\gamma \frac{\sqrt{(E^2 + \Gamma^2)}}{\pi T_c} \right) - \frac{\Gamma}{E} \tan^{-1} \frac{E}{\Gamma}$$

and  $g_d(0)$  is the density of the  $d$  state for a given spin direction at the Fermi energy,

$$g_d(0) = \frac{1}{\pi} \frac{\Gamma}{E^2 + \Gamma^2}. \quad (20)$$

The final result is the expression obtained by Zuckermann multiplied by the factor

$$1 + \alpha g_d(0) U_{\text{eff}}. \quad (21)$$

We see that there are two distinct contributions to the critical temperature change. The first one—which has been previously studied by Zuckermann—depends only on the resonance scattering. The relaxation time of the conduction electrons at the Fermi level due to this process is  $\tau_R(0)$  with

$$\frac{1}{2\tau_R(0)} = \frac{n_I}{\pi g(0)} \frac{\Gamma^2}{E^2 + \Gamma^2}.$$

$\tau_R(\omega)$  is related to the parameter  $\eta$  of  $\tilde{G}_{\omega}(k)$  by

$$\eta = 1 + \frac{1}{2\tau_R(\omega)|\omega|}.$$

Introducing the lifetime  $\tau_d$  of the virtual state

$$\tau_d = 1/2\Gamma,$$

one can write this first term

$$\left. \frac{\Delta T_c}{T_{c0}} \right|_R = -\alpha \frac{\tau_d}{\tau_R(0)}. \quad (22)$$

The second contribution, due to the Coulomb interaction which we have discussed in this paper, can be

written

$$\left. \frac{\Delta T_c}{T_{c0}} \right|_c = -\alpha^2 \frac{n_I}{g(0)} g_d^2(0) U_{\text{eff}}. \quad (23)$$

As shown in the Appendix, expression (22) is not changed when one takes into account the orbital degeneracy of the  $d$  states, if we define

$$\frac{1}{2\tau_R(0)} = \frac{n_I(2l+1)}{\pi g(0)} \frac{\Gamma^2}{E^2 + \Gamma^2}$$

and expression (23) has to be multiplied by  $(2l+1)$ .

## V. COMPARISON WITH EXPERIMENTS

### A. Experimental Results

The variation of the critical temperature  $T_c$  has been measured in dilute alloys of Al<sup>6,7</sup> and Zn.<sup>6</sup> Experimental results have been analyzed by the same authors within the theory of Markowitz and Kadanoff.<sup>10</sup> The decrease of  $T_c$  is due to two mechanisms: (1) the destruction of anisotropy of the gap; (2) a “valence effect” which, in this case, is due to the presence of localized states. From a theoretical point of view, there seems to be little interference between the two effects, as has been shown recently by Zuckermann and Singh<sup>11</sup> and Nagashima and Soda.<sup>12</sup>

#### 1. Aluminum Alloys

Figure 2 shows the observed initial decrease of  $T_c$  for the transition series. From these data, taking into account the destruction of the anisotropy of the gap, one obtains the effect of the resonant state. The results are given in Fig. 3 (taken from Ref. 6), where  $\rho$  is the residual resistivity ratio  $\rho = \tau_{273}/[\tau_R(0)]$  ( $\tau_{273}$  is the relaxation time at room temperature). The value relative to Al-Fe alloys is very doubtful (Fe has a very small solubility in Al).

#### 2. Zinc Alloys

In Zn, Cr and Mn impurities are magnetic. On the other hand, Fe, Co, and Ni impurities are nonmagnetic.

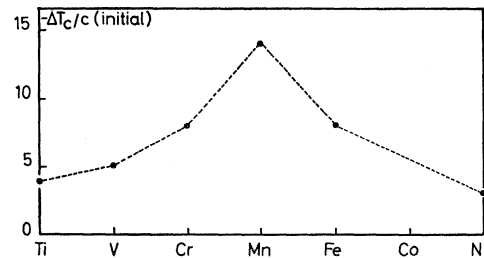


Fig. 2. Observed initial decrease of the transition temperature ( $c$  is the impurity concentration in at.%) (Refs. 6 and 7).

<sup>10</sup> D. Markowitz and L. P. Kadanoff, Phys. Rev. **131**, 563 (1963).

<sup>11</sup> M. J. Zuckermann and A. D. Singh (to be published).

<sup>12</sup> T. Nagashima and T. Soda, Progr. Theoret. Phys. (Kyoto) **36**, 1 (1966).

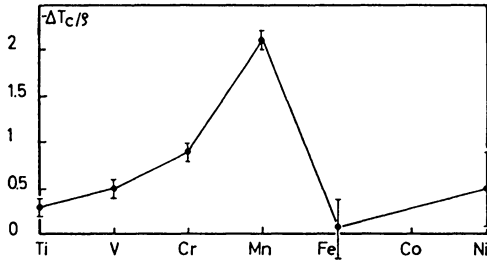


FIG. 3. Effect of the resonant state on the transition temperature as deduced from the experimental data by using a Markowitz-Kadanoff type of plot.

These results are in agreement with the discussion of Friedel<sup>2</sup> and show that the width of the virtual state should be smaller in Zn than in Al. For the nonmagnetic impurities with the same analysis, one obtains the following values of  $-\Delta T_c/\rho$  (taken from Ref. 6): 2.0 for Fe, 1.3 for Co, and 1.7 for Ni.

**B. Theoretical Interpretation**

Equation (23) can be written introducing the residual resistivity ratio:

$$-\frac{\Delta T_c}{\rho} = \alpha \frac{\tau_d}{\tau_{273}} T_{c0} [1 + \alpha g_d(0) U_{eff}]. \quad (24)$$

For numerical calculations, the Coulomb integral  $U$  has been taken equal to 10 eV (Anderson<sup>2</sup>). The width  $\Gamma$  of the state has been varied from 0.2 to 1 eV. Fig. 4 gives the ratio  $U_{eff}/U$  versus the number  $n_d$  of  $d$  electrons per state for different values of  $\Gamma$ . One can calculate  $1 + \alpha g_d(0) U_{eff}$ . The results are given in Fig. 5 for  $\Gamma = 1$  eV. The corresponding curves for other values of  $\Gamma$  have not been plotted for the sake of clarity; for  $\Gamma$  varying between 0.2 and 1 eV, the curves are similar (value equal to 1 for  $n_d = 0$  or 1; for  $n_d = 0.5$  there is a variation of a few percent). The factor  $1 + \alpha g_d(0) U_{eff}$  has small variations with  $\Gamma$ , but large variations with the occupation number  $n_d$ . This shows that the effect

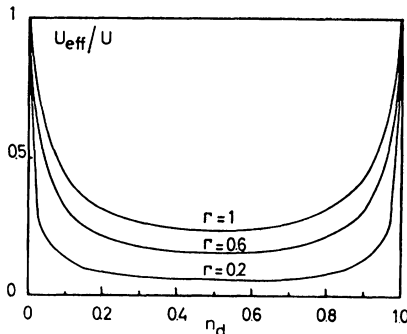


FIG. 4. Ratio of the effective potential  $U_{eff}$  and the Coulomb potential  $U$  versus the number of  $d$  electrons in each state  $n_d$ ; it is  $U = 10$  eV.

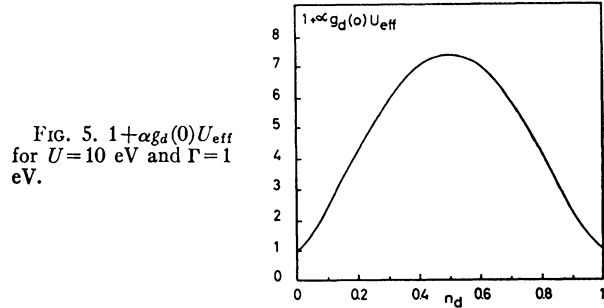


FIG. 5.  $1 + \alpha g_d(0) U_{eff}$  for  $U = 10$  eV and  $\Gamma = 1$  eV.

of Coulomb interaction can be very large (a factor 7.4 when  $n_d = 0.5$ )

From this, one can calculate  $-\Delta T_c/\rho$  as a function of  $n_d$  for various values of  $\Gamma$ . The results are plotted in Fig. 6 (solid lines). For comparison, the dashed curves represent the results without Coulomb interactions (Zuckermann's result):

$$-\frac{\Delta T_c}{\rho} = \alpha \frac{\tau_d}{\tau_{273}} T_{c0}.$$

The variation of the factor  $1 + \alpha g_d(0) U_{eff}$  drastically changes the results (by an order of magnitude).<sup>13</sup> One sees in Fig. 6 that there is a peak in the middle of the series for  $n_d \approx 0.5$ . The order of magnitude of  $-\Delta T_c/\rho$  is controlled by the value of  $\Gamma$ .

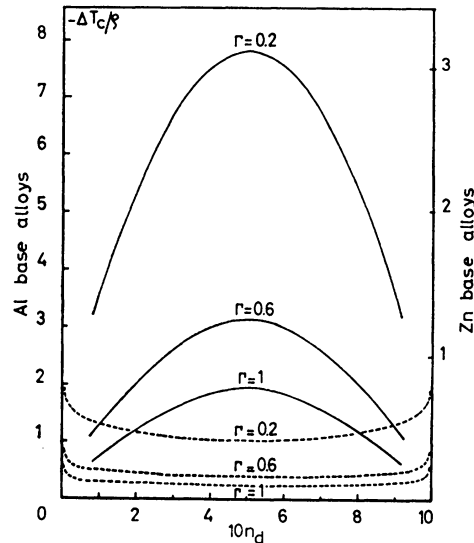


FIG. 6. Theoretical values of  $-\Delta T_c/\rho$  as a function of  $n_d$ . Solid line: with Coulomb interaction (our result). Broken line: without Coulomb interaction (Zuckermann's result).

<sup>13</sup> When  $n_d$  is very small or very near unity,  $-\Delta T_c/\rho$  becomes infinite. This is due to the coefficient  $\alpha$  which diverges as a consequence of the Lorentzian shape of the resonant state. This is a spurious effect which occurs only in the tail of  $g_d$ .

### 1. Aluminum Alloys

Without Coulomb interaction, one needs a value of  $\Gamma$  of the order of 0.1 eV and with large variations going from Ti to Mn and Ni. Such a small width cannot agree with the fact that these impurities are nonmagnetic.

On the contrary, if one takes into account Coulomb interaction, one explains the existence of the experimental peak (Fig. 3) for Mn ( $n_d \sim 0.5$ ) with values of  $\Gamma$  of the order of 1 to 1.5 eV. Such values agree with other estimations of the width and with the fact that all transitional impurities are nonmagnetic in Al. The experimental peak of Fig. 3 is narrower than the peak of Fig. 6. One cannot make a detailed comparison: The scattering problem is oversimplified by the model of localized states; the number  $n_d$  is roughly determined; the treatment of correlation through  $U_{eff}$  is valid only when  $n_d$  is sufficiently small or close to 1, and is not very good when  $n_d \approx 0.5$ .

### 2. Zinc Alloys

For these alloys, we have only three points (Fe, Co, Ni). One can estimate the width:  $\Gamma$  is of the order of 0.2 to 0.4 eV. This smaller width (compared to the case of Al alloys) agrees with the occurrence of magnetism for impurities in the middle of the transitional series (Cr and Mn).

## ACKNOWLEDGMENTS

The authors would like to thank Professor G. Boato for helpful discussions on the experimental results, Dr. M. J. Zuckermann for a stimulating correspondence on the subject, and Dr. G. Böbel for many interesting discussions.

## APPENDIX: GENERALIZATION TO THE DEGENERATE $d$ LEVEL CASE

Anderson's Hamiltonian for a degenerate  $d$  level is

$$H_0 = \sum_k \epsilon_k n_k + \sum_\alpha \epsilon_\alpha n_\alpha,$$

$$H_1 = \sum_{k\alpha} (V_{\alpha k} a_{\alpha^\dagger} a_k + V_{k\alpha} a_k^\dagger a_\alpha),$$

$$H_2 = \frac{1}{2} U \sum_{\alpha\beta} n_\alpha n_\beta + \frac{1}{2} (U - J) \sum_{\alpha \neq \beta} n_\alpha n_\beta + \frac{1}{2} \sum_{k,k'} \lambda_{k,k'} a_k^\dagger a_{-k}^\dagger a_{-k'} a_{k'},$$

where  $J$  is the exchange integral and  $\alpha, \beta = 1, 2, \dots, 2l+1$ ,  $l$  being the  $d$ -state angular moment (i.e.,  $l=2$  for transition-metal impurities).

We are still treating the nonmagnetic case and, therefore, because of the perturbation, each level is shifted to the energy

$$E = \epsilon_d + \langle n \rangle [(2l+1)U + 2l(U-J)]$$

and spread out into a virtual level of half-width  $\Gamma$ .

We will not work out all the details of the various calculations, but simply give a few results and comments. First of all, we want to point out that we cannot take into account the correlation of electrons with the same spin, i.e., we have to treat the part of the Hamiltonian relative to electrons with parallel spin completely in the framework of the Hartree-Fock approximation.

This feature arises since we are studying a superconductivity problem and hence the pairing of states with opposite spin.

In other words, when linearizing the equations of motion, we can make the following factorization for antiparallel spins:

$$\frac{1}{2} U (\langle a_\alpha^\dagger a_{-\beta}^\dagger \rangle a_{-\beta} + \langle a_{-\beta}^\dagger a_{-\beta} \rangle a_\alpha^\dagger);$$

however, for the parallel spins, we get only

$$\frac{1}{2} (U - J) \langle a_\beta^\dagger a_\beta \rangle a_\alpha^\dagger.$$

In the ladder approximation used by Schrieffer and Mattis, the repeated exchange interaction between electrons of the same spin is included in the calculation of the self-energy, and these correlation effects are taken into account.

In this topic,  $V_{k\alpha}$  are different for different  $\alpha$  and different  $k$  directions. We can choose the localized orbitals in such a way that the average of  $V_{k\alpha}$  over the modulus of  $k$  may be written

$$V(4\pi)^{1/2} Y_l^\alpha(\theta, \phi),$$

where  $Y$  is a spherical harmonic and  $\theta$  and  $\phi$  give the direction of  $k$ .

Because of this structure, we have

$$\langle V_{\alpha k} V_{k\beta} \rangle = \delta_{\alpha\beta} |V|^2,$$

$$\sum_{\alpha\beta} \langle V_{k\alpha} V_{\alpha k'} V_{k'\beta} V_{\beta k} \rangle = (2l+1) |V|^4,$$

where the average is made with respect to the electron momenta. Using these properties, we can generalize all our results, substituting, for the products of the admixture parameters, their averages.

In particular,

$$\Gamma = \pi g(0) |V|^2$$

is the half-width of every virtual level, and

$$\sum_k V_{\alpha k} G_\omega^0(k) V_{k\beta} = \delta_{\alpha\beta} i \frac{\omega}{|\omega|} \Gamma,$$

$$\tilde{G}_\omega(\alpha, \beta) = \delta_{\alpha\beta} \tilde{G}_\omega(\alpha).$$

In the normal alloy, the averaged Green's functions are

$$\tilde{G}_\omega(k) = 1/(i\omega\eta_l - \epsilon_k),$$

$$\tilde{G}_\omega(d) = 1/(i\omega\chi - E),$$

with

$$\eta_l = 1 + n_l (2l+1) \frac{|V|^2 \chi}{\omega^2 \chi^2 + E^2}.$$



and

$$\chi = 1 + \Gamma/|\omega|.$$

In the same way, we obtain

$$\tilde{G}_\omega(k, \alpha) \tilde{G}_{-\omega}(-k, -\beta) = \delta_{\alpha\beta} S_\omega(k, \alpha)$$

and

$$\frac{1}{|\lambda|} = T_c \sum_\omega \sum_{kk'} \left[ S_\omega(k, k') - n_I(2l+1) \frac{U}{1 + UT_c \sum_{\omega j} S_\omega(i, j)} \right. \\ \left. \times T_c \sum_{\omega'} S_{\omega'}(k, i) S_\omega(i, k') \right].$$

Now, we have

$$\sum_k^D \sum_{k'}^D S_\omega(k, k') \sim \frac{2g(0)}{|\omega|} \tan^{-1} \frac{\omega_D}{|\omega|} - (2l+1)n_I \\ \times \frac{\Gamma}{|\omega| [E^2 + (|\omega| + \Gamma)^2]} + O(r^2)n,$$

$$\sum_k^D S_\omega(k, d) \sim \frac{1}{|\omega| [E^2 + (|\omega| + \Gamma)^2]} + O(n_I),$$

$$\sum_j S_\omega(i, j) \sim \frac{1}{E^2 + (|\omega| + \Gamma)^2} + O(n_I).$$

In that case, the relaxation time  $\tau_R(0)$  is given by

$$\frac{1}{2\tau_R(0)} = \frac{n_I(2l+1)}{\pi g(0)} \frac{\Gamma^2}{E^2 + \Gamma^2}.$$

We can write, exactly as in the nondegenerate case,

$$\frac{\Delta T_c}{T_{c0}} \simeq -\alpha \frac{\tau_d}{\tau_R(0)} [1 + \alpha g_d(0) U_{\text{eff}}].$$

## Sublattice Magnetization in Yttrium and Lutetium Iron Garnets\*

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The temperature dependence of the *a* and *d* sublattice magnetization in yttrium iron garnet (YIG) and lutetium iron garnet (LuIG) has been observed by means of the NMR of  $\text{Fe}^{57}$  between 4 and 373°K, with special emphasis on the temperature range where the spin-wave theory is expected to hold. An analysis of these results in terms of the spin reversals due to acoustical and optical spin-wave modes has been carried out. From a comparison of theory and experiment in YIG, the value of the dispersion parameter  $D = 30.0 \pm 0.6 \text{ cm}^{-1}$  is obtained. A reasonable estimate of the separate exchange parameters is  $J_{ad} = 22.5 \pm 1 \text{ cm}^{-1}$ ,  $J_{aa} = 2.0 \pm 0.5 \text{ cm}^{-1}$ , and  $J_{dd} = 0.5 \pm 0.5 \text{ cm}^{-1}$ , subject to the constraint that their linear combination gives  $D = 30 \text{ cm}^{-1}$ . The agreement between experiment and theory is improved when a small transferred hyperfine interaction from the *d* sites to the *a* sites (and vice versa) is postulated. For LuIG one obtains a value  $D = 27.3 \text{ cm}^{-1}$ . The values of *D* and of the exchange parameters  $J_{ij}$  for YIG and LuIG are compared with those from other experiments. In YIG, the magnetic field dependence of the sublattice magnetizations has been observed up to 10 kG at 63 and 77°K, and there is good agreement with the results from spin-wave theory. It is believed that this is the first such investigation in a ferrimagnet. In the course of these experiments, the gyromagnetic ratio of  $\text{Fe}^{57}$  was determined to be  $\gamma/2\pi = 137.4 \pm 0.2 \text{ Hz/G}$ . In LuIG a broad spectrum of resonances between about 40 and 76 MHz was observed at 4.2°K. This is attributed to the resonance of  $\text{Lu}^{175}$  and  $\text{Lu}^{176}$  in a transferred hyperfine field ( $\sim 100 \text{ kG}$ ) broadened by quadrupole interaction. In  $\text{Y}^{89}$  in YIG, this transferred field seems to be smaller than  $\sim 10 \text{ kG}$ , from NMR and specific-heat evidence.

### I. INTRODUCTION

IN recent years there have been several accurate investigations of the sublattice and total magnetizations in ordered magnetic materials at low tem-

peratures.<sup>1-3</sup> The purpose was to test the spin-wave theory and to derive the respective exchange parameters in the material under investigation. In this paper

<sup>1</sup> H. L. Davis and A. Narath, *Phys. Rev.* **134**, A433 (1964); A. J. Heeger and T. W. Houston, *ibid.* **134**, A661 (1964).

<sup>2</sup> B. E. Aigyle, S. H. Charap, and E. W. Pugh, *Phys. Rev.* **132**, 2051 (1963).

<sup>3</sup> See, for instance, V. Jaccarino, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic Press Inc., New York, 1965), Vol. IIA, p. 307; A. M. Portis and R. H. Lindquist, *ibid.*, p. 357.

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