Nonmagnetic Localized Impurity States in Dilute Superconducting Alloys*

U. N. UPADHYAYA AND K. P. SINHA

National Chemical Laboratory, Poona, India

(Received 13 November 1967)

The effect of magnetic-element impurities in a virtual nonmagnetic state on the superconducting transition temperature T_c of dilute alloys is discussed. It is found that, in general, one-body-type interactions between conduction (s) electrons of the host metal and the d electrons of the impurity atoms tend to decrease T_c, whereas the two-body type of interactions between s and d electrons can enhance T_c under certain conditions. It appears that the additional attractive electronic interaction, in contradistinction to the phonon-induced mechanism, between electrons of the BCS pairs is a consequence of a proper cognizance of the instantaneous two-body interaction between conduction and impurity electrons.

1. INTRODUCTION

IN recent years, the effects of magnetic-element impurities in metals have been of considerable interest both from theoretical and experimental viewpoints. The absence or presence of magnetic moments and associated electronic properties, e.g., electronic transport, magnetic susceptibility, low-temperature specific heats, anomalous thermoelectric power, and the superconducting transition temperatures (T_c), have been extensively studied. The theoretical models considered, in this context, are those due to Anderson,[1] Wolff,[2] Kondo,[3] Abrikosov and Gorkov,[4] Shul,[5] and others.[6] In Anderson's model one takes into account the mixing between conduction (s) electron states and localized d states of the impurities through an average Hartree-Fock field (one-body effects) along with the two-body d-d Coulomb interaction (correlation energy). This mixing comes from interatomic matrix elements of the Hartree-Fock potentials connecting Wannier functions centered at two different atoms.

Kondo's treatment makes use of the usual s-d exchange interaction and has been very successful in explaining the electronic transport properties for systems having net localized moments at the impurities. Abrikosov and Gorkov[4] have shown that the interaction between conduction electrons and impurity spins involving a spin-dependent Hartree-Fock potential leads to nonconservation of the conduction-electron spin, which in turn affects the formation of Cooper pairs. Thus they predicted the lowering of T_c with the introduction of paramagnetic impurities in some metals. They also predicted gapless superconductivity.

Schrieffer and Wolff[7] have recently shown the equivalence of the Hamiltonians considered by Kondo and Anderson for the situation where there is a net magnetic moment (small s-d mixing case). However, this equivalence was found to be valid only for the antiferromagnetic s-d exchange interaction. Furthermore, as the one-body Hartree-Fock potential, whether spin-independent or spin-dependent is at best an average effect of the many-body s-d interaction, it cannot adequately represent the exact many-body effects arising from the two-body Coulomb interactions. Indeed, it has been shown earlier[6,8] that indirect Coulomb and exchange-type interactions involving conduction and d electron states give rise to additional attractive interactions between electrons of the BCS pairs under certain conditions. It should be noted that Ganguly, Upadhyaya, and Sinha[6] considered generalized interactions involving localized impurity states in conjunction with phonon-induced process. Geilikman took the usual s-d Coulomb and exchange processes involving s and d bands in some pure metals.

In what follows, we analyze the effects of all one-body and two-body interaction on the transition temperature of some superconductors.

2. SUPERCONDUCTING TRANSITION TEMPERATURE

The total change in the superconducting transition temperature of a system can be written as

$$\Delta T_c{}^t/T_c{}^0=(\Delta T_c{}^{\mathrm{I}}+\Delta T_c{}^{\mathrm{II}}+\Delta T_c{}^{\mathrm{III}})/T_c{}^0, \qquad (1)$$

where[6]

$$k_B T_c{}^{\mathrm{I}}=1.14\langle\hbar\omega\rangle \exp[-1/N(0)V_{\mathrm{eff}}], \qquad (2)$$

with

$$V_{\mathrm{eff}}=V_{\mathrm{ph}}+\xi W,$$
$$W=W_1+W_2. \qquad (3)$$

V_{ph} is the strength of the phonon-induced electron-

* Communication No. 1152 from the National Chemical Laboratory, Poona-8, India.

[1] P. W. Anderson, Phys. Rev. **124**, 41 (1961); see this paper also for earlier works.

[2] P. A. Wolf, Phys. Rev. **124**, 1030 (1961).

[3] J. Kondo, Progr. Theoret. Phys. (Kyoto) **32**, 37 (1964).

[4] A. A. Abrikosov and L. P. Gorkov, Zh. Eksperim. i Teor. Fiz. **39**, 1781 (1960) [English transl.: Soviet Phys.—JETP **12**, 1243 (1961)].

[5] H. Suhl, Phys. Rev. Letters **19**, 442 (1967).

[6] N. B. Ganguly, U. N. Upadhyaya, and K. P. Sinha, Phys. Rev. **146**, 317 (1966) and papers referred to therein.

[7] J. R. Schrieffer and P. A. Wolff, Phys. Rev. **149**, 491 (1966).

[8] B. T. Geilikman, Usp. Fiz. Nauk **88**, 327 (1966) [English transl.: Soviet Phys.—Usp. **9**, 142 (1966)].

electron interaction,[9] W_1 and W_2 are the attractive interactions emanating from the two-body effects discussed earlier.[6] ξ is the impurity concentration, $N(0)$ is the density of states at the Fermi surface, $\langle\hbar\omega\rangle$ is the average phonon energy. T_c^{II} is the transition temperature calculated by Suhl and Matthias,[10] who considered only the intraband spin-independent potential scattering due to impurities. The explicit expression is given by

$$k_B T_c^{II} = \frac{\langle\hbar\omega\rangle}{1.75}\left[\frac{\epsilon_0(\text{pure})}{\langle\hbar\omega\rangle}\right]^{(4\pi w^2\xi N(0)/\langle\hbar\omega\rangle)}. \quad (4)$$

Here ϵ_0(pure) is the energy-gap parameter for the pure system and w is the interaction parameter of Eq. (30) of Suhl and Matthias. T_c^{III} is the transition temperature obtained by Ratto and Blandin[11] (see also Zuckerman[12]), where they have incorporated the effect arising from Anderson-type valence effect which includes s-d mixing (one-body effect) and correlation between d electrons.

The explicit forms of W_1 and W_2 are[6]

$$W_1 = (2/\Delta_{\lambda l})(|U-V|^2 + |U|^2 - 2|V|^2), \quad (5)$$

$$W_2 = \tfrac{1}{4}[G^2/(\epsilon_\lambda - \epsilon_F)], \quad (6)$$

where U and V are the two-body Coulomb and exchange-type interactions involving empty localized impurity states (λ), l the occupied impurity state, and the conduction-electron states. G is the two-body Coulomb-type integral describing simultaneous transfer of two conduction electrons to impurity state λ. ϵ_λ is the one electron energy of the state inclusive of the correlation energy, ϵ_F is the Fermi energy, and $\Delta_{\lambda l} \sim \epsilon_\lambda - \epsilon_l$ is the excitation energy for the impurity electron.

It would be expedient to expand $\Delta T_c = T_c - T_c^0$ in terms of impurity concentration ξ for each process. Thus, for low-concentration regions and retaining terms up to second order in ξ, we get

$$\Delta T_c^{I}/T_c^0 = a_I\xi + b_I\xi^2, \quad (7)$$

with

$$a_I = -(W/V_{ph})\ln(k_B T_c^0/1.14\langle\hbar\omega\rangle), \quad (8)$$

$$b_I = \left(\frac{W}{V_{ph}}\right)\ln\left(\frac{k_B T_c^0}{1.14\langle\hbar\omega\rangle}\right)\left[\tfrac{1}{2} + \ln\left(\frac{k_B T_c^0}{1.14\langle\hbar\omega\rangle}\right)\right]. \quad (9)$$

It has been shown earlier[6] that a_I and b_I are positive definite quantities and thus ΔT_c^{I} always gives an increase in T_c. On the other hand, the potential-scattering[10] part takes the form[6]

$$\Delta T_c^{II}/T_c^0 = -a_{II}\xi - b_{II}\xi^2, \quad (10)$$

with

$$a_{II} = -\frac{4w^2N(0)}{\langle\hbar\omega\rangle}\ln\left(\frac{\epsilon_0(\text{pure})}{\langle\hbar\omega\rangle}\right), \quad (11)$$

$$b_{II} = \frac{8w^2[N(0)]^2}{[\langle\hbar\omega\rangle]^2}\ln\left(\frac{\epsilon_0(\text{pure})}{\langle\hbar\omega\rangle}\right)\left[1+\ln\left(\frac{\epsilon_0(\text{pure})}{\langle\hbar\omega\rangle}\right)\right]. \quad (12)$$

As $\langle\hbar\omega\rangle$ is much larger than energy-gap parameter ϵ_0(pure), it can be seen that a_{II} and b_{II} are again positive-definite quantities, and the second process [cf. Eq. (10)] will always lead to reduction of transition temperature. Finally, the contribution from the valence effect due to one-body s-d mixing is expressed as[11]

$$\Delta T_c^{III}/T_c^0 = -\alpha[N_d(0)/N(0)][1+\alpha N_d(0)U_{eff}]\xi, \quad (13)$$

with

$$\alpha = \ln\left[2\gamma\frac{(E^2+\Gamma^2)^{1/2}}{\pi T_c}\right] - \frac{\Gamma}{E}\tan^{-1}\frac{E}{\Gamma}, \quad (14)$$

where $N_d(0)$ is the density of the d state for a given spin direction at the Fermi surface and U_{eff} is the effective correlation energy between the localized d states. Further, Γ is the half-width of the virtual d states, $\gamma = 0.577$ the Euler's constant and E is the energy corresponding to the peak of the resonant d level. According to Ratto and Blandin,[11] the factor $\alpha N_d(0)U_{eff}$ has a maximum value 6.4 for n_d (number of d electrons per state) equal to 0.5. However it becomes almost zero for $n_d = 0$ or 1. It turns out that α, for their choice of Γ and E, is always a positive quantity. Therefore T_c^{III} will give a negative contribution.

3. DISCUSSION

The over-all change in transition temperature is thus the sum total of all these distinct processes [cf. Eq. (1)]. The changes ΔT_c^{II} and ΔT_c^{III} tend to decrease the transition temperature whereas the contribution ΔT_c^{I} will increase it. Accordingly, the net change will depend on the relative magnitude of these quantities.

The foregoing study suggests that the one-body interaction terms always lead to a decrease in T_c whether it is due to intraband potential scattering or valence effect involving resonant s-d mixing. On the other hand, the generalized two-body interaction gives an attractive electron-electron term over and above phonon-induced BCS term and thus leads to an enhancement of T_c. A necessary prerequisite for this additional electronic interaction is that the impurities are in the nonmagnetic state and there are virtual states above and below the Fermi level.

It seems that for systems containing transition-metal impurities in Al[13] and Zn, the contributions from one-body processes (ΔT_c^{II} and ΔT_c^{III}) dominate the two-body effects (ΔT_c^{I}) and there is a net decrease

[9] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).
[10] H. Suhl and B. T. Matthias, Phys. Rev. **114**, 977 (1959).
[11] C. F. Ratto and A. Blandin, Phys. Rev. **156**, 513 (1967).
[12] M. J. Zuckerman, Phys. Rev. **140**, A889 (1965).
[13] R. Aoki and T. Ohtsuko, J. Phys. Soc. Japan **23**, 955 (1967).

in T_c. On the other hand, as reported earlier[14,15] some transition metals (e.g., Ti and Zr) containing magnetic-element impurities in nonmagnetic state seem to exhibit increase in T_c. This would suggest that the two-body effects dominate the one-body interaction over certain impurity-concentration regions in these systems.

Such two-body interactions have also been found to be important for other physical properties, e.g., resistance minimum in alloys[16] and semiconductors[17] containing impurities, thermoelectric power,[18] and anomalous density of states,[19] etc.

Recently, Fowler *et al.*[20] have discovered a positive isotope effect in α-uranium which suggests a mechanism for superconductivity other than that involving lattice deformation. This mechanism would involve an interaction of the conduction electrons with the electron cores resulting in the polarization of d (or f) electron shells. The mechanism considered by us,[6] in conjunction with the phonon-induced process, may describe such electronic polarization effects in pure systems as well.

[14] J. A. Cape and R. R. Hake, Phys. Rev. **139**, A142 (1965).
[15] B. T. Matthias, V. B. Compton, H. Suhl, and E. Cornzwit, Phys. Rev. **115**, 1597 (1959).
[16] B. N. Ganguly, U. N. Upadhyaya, and K. P. Sinha, Proc. Phys. Soc. (London) **90**, 445 (1967).
[17] K. S. V. L. Narasimhan and K. P. Sinha, Can. J. Phys. **45**, 3029 (1967).
[18] U. N. Upadhyaya and K. P. Sinha (to be published).
[19] B. N. Ganguly, Phys. Letters **25A**, 262 (1967).
[20] R. D. Fowler, J. D. G. Lindsay, R. W. White, H. H. Hill, and B. T. Matthias, Phys. Rev. Letters **19**, 892 (1967).

PHYSICAL REVIEW VOLUME 169, NUMBER 2 10 MAY 1968

Millimeter-Wave Mixing with Josephson Junctions

C. C. GRIMES AND SIDNEY SHAPIRO*
Bell Telephone Laboratories, Murray Hill, New Jersey
(Received 3 November 1967)

Experiments are reported in which two millimeter-wave signals incident on point-contact Josephson junctions produced changes in the junction dc voltage versus current characteristic and an intermediate frequency output whose amplitude depended sensitively on both junction bias and applied power. Equations are derived, based on Josephson's phenomenological equations, for the Josephson current in a junction exposed to two applied rf signals. When the applied signals differ appreciably in frequency, additional constant-voltage steps in the V-I curve are predicted which are spaced at the difference frequency. These steps have been observed in experiments employing sources at 64 and 72 Gc/sec. Results of mixing experiments utilizing two sources nearly equal in frequency are reported at 23 and at 72 Gc/sec. In this case the two waves beat together and are equivalent in their effect to a single signal amplitude modulated at the difference frequency. Also explained on the same basis are experiments in which the third harmonic of a signal at 24 Gc/sec mixed with a signal at 72 Gc/sec. These results demonstrate the existence of the Josephson mixing mechanism as opposed to classical nonlinear mixing, and they show that it is operative at microwave and millimeter-wave frequencies over a wide range of power.

I. INTRODUCTION

A LARGE number of high-frequency effects have been demonstrated by Josephson junctions[1,2] formed from superconducting point contacts.[3] Radio-frequency[4] and microwave[4,5] generation; microwave harmonic generation[6]; rf,[7] microwave,[8,9] and far-infrared[8,9] video detection have all been reported. In this paper we report the first extensive study of millimeter-wave mixing with point-contact Josephson junctions.

Two signals, either in the vicinity of 23 Gc/sec (13-mm wavelength) or in the vicinity of 72 Gc/sec (4-mm wavelength), were mixed in the Josephson junction. The mixing action was detected both by observing the difference-frequency signal directly and by observing modification of the dc voltage-current characteristic of the junction.

* Present address: Department of Electrical Engineering, University of Rochester, Rochester, N.Y. 14627.
[1] B. D. Josephson, Phys. Letters **1**, 251 (1962); Rev. Mod. Phys. **36**, 216 (1964); Advan. Phys. **14**, 419 (1965).
[2] P. W. Anderson, in *Lectures on the Many-Body Problem*, edited by E. R. Caianiello (Academic Press Inc., New York, 1964), p. 113; and in *Progress in Low Temperature Physics*, edited by C. J. Gorter (North-Holland Publishing Co., Amsterdam, 1967), Vol. V, p. 1.
[3] J. E. Zimmerman and A. H. Silver, Phys. Rev. **141**, 367 (1966).
[4] J. E. Zimmerman, J. A. Cowen, and A. H. Silver, Appl. Phys. Letters **9**, 353 (1966).
[5] A. H. Dayem and C. C. Grimes, Appl. Phys. Letters **9**, 47 (1966).
[6] S. Shapiro, J. Appl. Phys. **38**, 1879 (1967).
[7] A. H. Silver and J. E. Zimmerman, Appl. Phys. Letters **10**, 142 (1967).
[8] C. C. Grimes, P. L. Richards, and S. Shapiro, Phys. Rev. Letters **17**, 431 (1966).
[9] C. C. Grimes, P. L. Richards, and S. Shapiro (to be published).