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Josephson effect between superconductors in possibly different spin-pairing states

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The Josephson current between two weakly coupled superconductors of which one has pairs in a spin-triplet state is considered. It is shown that under quite general conditions there is no Josephson effect up to second order in the transition-matrix elements between a superconductor with spin-triplet pairs and one with spin-singlet pairs. This offers a possibility to investigate experimentally whether a particular superconductor has spin-triplet pairs by coupling it weakly to a well-known spin-singlet pairing superconductor. Some superconducting materials which have been suggested earlier as possibly having spin-triplet pairs to account for their measured properties are investigated by forming junctions with a niobium point and looking at the Josephson effect. It turns out that all these junctions behave normally as far as the ac Josephson effect is concerned. We therefore provide strong experimental evidence that the investigated materials, viz., U_6Fe, Th_7Co_3, Th_7Fe_3 $CeRu_2$, $Ce_{1-x}Gd_xRu_2$, Zr_2Co, and Zr_2Ni, are singlet superconductors.

I. INTRODUCTION

In the microscopic theory of superconductivity, as given by Bardeen, Cooper, and Schrieffer[1] and Gorkov,[2] electrons are supposed to condense in pairs in which these electrons have both opposite wave vectors and spins. The pair states are symmetric in the interchange of the $\vec{k}$ vectors of the individual electrons and antisymmetric in the interchange of their spins. The spin-singlet character follows in fact from the assumption that the attractive electron-electron interaction $V(\vec{k},\vec{k}')$ is independent of the angle between $\vec{k}$ and $\vec{k}'$. However, in expanding this interaction in spherical harmonics, terms of even as well as odd parity may arise. Terms of even parity will favor spin-singlet pair formation, whereas odd-parity terms may lead to spin-triplet pair formation. Anderson and Morel[3] discussed the latter possibility in connection with superfluidity of ^{3}He. They consider the equal-spin-pairing (ESP) state in which the pairs have a total spin projection along a particular direction equal to ± 1. Because of the introduction of this special direction the resulting superfluid is anisotropic. The energy gap $\Delta_{\vec{k}}$ is found to depend on the direction of $\vec{k}$. Balian and Werthamer[4] (BW) considered triplet pairs with spin projections $+1$, 0, and -1 along a particular direction. Their more general treatment leads to a ground state with a lower energy than the ESP state, with the energy-gap function $\Delta_{\vec{k}}$ being independent of the direction of $\vec{k}$.

Spin-triplet pairing states of both the ESP and BW type are very likely to occur in the superfluid phases of liquid ^{3}He.[5,6] A still unanswered question concerns the possible occurrence of spin-triplet pairing in superconductors. Since about 1960 a number of possible "triplet superconductors," have been suggested, for reasons to be discussed later on in this paper. However, as has been thoroughly discussed by BW[4] it is very difficult to find an experimental setup from which the type of spin pairing follows in an unambiguous way. It is the purpose of this paper to discuss a new method, not considered by BW. The method is based on the theoretical observation that Josephson effects should depend in a very characteristic way on the type of spin pairing of the two weakly coupled superconductors.

In Sec. II it is shown that the Josephson current between two weakly coupled superconductors vanishes in the case where one superconductor is in a spin-singlet state and the other in a spin-triplet state. This turns out to be also the case if in the barrier paramagnetic impurities are present with the ability to flip the electron spins. This yields an experimental means of proving the existence of spin-triplet pairing for a particular superconductor with the help of the ac Josephson effect. In Sec. III some superconductors, previously mentioned in the literature as possible triplet superconductors, are recalled together with the arguments on the grounds of which it was suggested they were in a triplet state. Section IV deals with the experiments we have performed. The conclusions are given in Sec. V.

II. JOSEPHSON CURRENT BETWEEN A SINGLET AND A TRIPLET SPIN-PAIRING SUPERCONDUCTOR

We describe the weak coupling between the two superconductors with the spin-conserving tunneling Hamiltonian H_T introduced by Cohen *et al.*[7]

$$H_T=\sum_{\vec{k}_1\vec{k}_2\sigma} T_{\vec{k}_1\vec{k}_2}\, a^{\dagger}_{\vec{k}_1\sigma} a_{\vec{k}_2\sigma}+\text{H.c.} \qquad (1)$$

in which a and $a^\dagger$ are annihilation and creation operators and the wave vectors $\vec{k}_1$ and $\vec{k}_2$ belong to electrons from superconductors 1 and 2, respectively.

It follows from time-reversal symmetry that

$$T^*_{\vec{k}_1,\vec{k}_2} = T_{-\vec{k}_1,-\vec{k}_2}\,. \tag{2}$$

If we now suppose that superconductor 1 is a singlet-pairing superconductor which is weakly coupled to the triplet-pairing superconductor 2, we can derive that[8] the phase-dependent contributions to the current,[9] the pair current I_p, and the quasiparticle-pair interference current I_{qpp} are zero in second order in the tunneling-matrix elements. This result is independent of the specific triplet state in which one of the superconductors condenses. The argument is as follows. Suppose first that the triplet superconductor condenses in the ESP state of Anderson and Morel. The phase-dependent currents I_p and I_{qpp} originate in a calculation along the same lines as given by Josephson[10] from a number of terms in the perturbation expression in which the expectation value of two creation operators in one superconductor is combined with the expectation value of two annihilation operators in the other superconductor. A typical term contributing to the current is

$$\frac{e}{\hbar^2}\int_{-\infty}^{t} e^{\eta t'}dt' \sum_{\vec{k}_1\vec{k}_2\sigma\sigma'} |T_{\vec{k}_1\vec{k}_2}|^2 \langle a^\dagger_{\vec{k}_1\sigma}(t)a^\dagger_{-\vec{k}_1\sigma'}(t')\rangle \times\langle a_{\vec{k}_2\sigma}(t)a_{-\vec{k}_2\sigma'}(t')\rangle, \tag{3}$$

where $\eta \to +0$. The other terms in the expression for the phase-dependent current differ only in the interchange of t and t' and/or the interchange of creation and annihilation operators. If we suppose superconductor 1 to be in a spin-singlet state the expectation value $\langle a^\dagger_{\vec{k}_1\sigma}a^\dagger_{-\vec{k}_1\sigma'}\rangle$ is different from zero only if σ and σ' are opposite spin components. The value $\langle a_{\vec{k}_2\sigma}a_{-\vec{k}_2\sigma'}\rangle$ for the triplet-superconductor is in general also different from zero for $\sigma \neq \sigma'$ except in an ESP state. So for an ESP superconductor 2 every term in the sum of expression (3) is zero and consequently no phase-dependent current results. However, this result can also be derived in the more general case. The wave function of a singlet-pairing superconductor is symmetric in the interchange of the space coordinates of the electrons forming a pair. This interchange is equivalent to a reversal of sign of the two wave vectors $\vec{k}$ and $-\vec{k}$ attributed to the electrons in this pair. The wave function is antisymmetric in the interchange of spins in the pair. For a triplet superconductor it is precisely the other way around. These symmetry properties imply the following properties for the expectation values:

singlet:

$$\begin{aligned}\langle a^\dagger_{\vec{k}_1\uparrow}(t)a^\dagger_{-\vec{k}_1\downarrow}(t')\rangle &= \langle a^\dagger_{-\vec{k}_1\uparrow}(t)a^\dagger_{\vec{k}_1\downarrow}(t')\rangle \\ &= -\langle a^\dagger_{\vec{k}_1\downarrow}(t)a^\dagger_{-\vec{k}_1\uparrow}(t')\rangle\,,\end{aligned}$$

triplet:

$$\begin{aligned}\langle a_{\vec{k}_2\uparrow}(t)a_{-\vec{k}_2\downarrow}(t')\rangle &= -\langle a_{-\vec{k}_2\uparrow}(t)a_{\vec{k}_2\downarrow}(t')\rangle \\ &= \langle a_{\vec{k}_2\downarrow}(t)a_{-\vec{k}_2\uparrow}(t')\rangle\,.\end{aligned} \tag{4}$$

Applying these symmetry properties and taking into account time-reversal symmetry as expressed in Eq. (2), we observe that terms in expression (3) with wave vectors $\vec{k}_1, \vec{k}_2$ and $-\vec{k}_1, -\vec{k}_2$ cancel out. Therefore the total phase-dependent current in second order is zero in the case of tunneling between a singlet-pairing and a triplet-pairing superconductor. It should be emphasized that this conclusion has been derived using the spin-conserving tunnel Hamiltonian H_T of Eq. (1). However, the spin-conserving character of the tunneling process may be doubtful if for instance paramagnetic impurities were to occur in the tunneling barrier. This is certainly not unlikely in the case of a number of candidates for triplet superconductivity containing magnetic ions like Fe, Co, Ni, or Mn. Exchange scattering of a tunneling electron on a magnetic impurity can result in a spin flip of the tunneling electron. In the Appendix it is shown that a spin-nonconserving character of the tunneling process caused by magnetic impurities in the tunneling barrier with random magnetic moments does not alter the conclusion that there is no Josephson current in second order for tunneling between a singlet and a triplet superconductor. This conclusion cannot be drawn if the magnetic impurities have, due to mutual interaction, an average spin component not equal to zero along a particular direction. Also in the case that the magnetic impurities would be in some way connected with or partly responsible for the occurrence of triplet superconductivity the above conclusion may not hold. The next-higher-order term in the current expression is of fourth order in the tunneling-matrix elements. It may contain phase-dependent terms not canceling out and may therefore give rise to a fourth-order Josephson effect. The ac effects arising from nonvanishing terms of this kind, however, will not satisfy the usual Josephson relation[11]

$$\frac{d\phi}{dt} = \frac{2eV}{\hbar} \tag{5}$$

in which ϕ is the phase difference between the two superconductors and V the applied voltage across the junction. A careful analysis shows that in fourth order of the matrix elements the phase relation becomes

$$\frac{d\phi}{dt} = \frac{4eV}{\hbar} . \tag{6}$$

Josephson effects connected with a factor of 2 in the dependence of $d\phi/dt$ on the applied voltage V [Eq. (5)] will therefore not occur in tunneling between a triplet and a singlet superconductor under quite general conditions. The occurrence or absence of Josephson effects connected with this factor of 2 therefore yields experimental evidence as to whether the two superconductors are in the same or in a different spin state. If the potential between the electrons causing superconductivity is expanded in spherical harmonics, attractive terms of even and odd parity may be present. In principle, therefore, there is a possibility that pairs of mixed singlet and triplet character will form. An explicit mathematical example has been worked out by Werthamer *et al.*[12] BW[4] also discuss this possibility. These authors conclude that the existence of pairs with mixed s- and p-wave character, although mathematically possible, is physically very unlikely. However, for such a mixed state none of the two symmetry relations (4) holds and strictly speaking the actual presence of a Josephson frequency relation (5) with a factor of 2 only proves that both superconductors do not have pairs in a *purely* opposite type of symmetry (i.e., singlet and triplet).

III. DISCUSSION OF INDICATIONS OF TRIPLET PAIRING IN SOME SUPERCONDUCTORS

The possible occurrence of spin-triplet pairing in superconductors has been the subject of both theoretical and experimental studies.

Privorotskii[13] suggests on theoretical grounds that triplet-pairing superconductivity might occur in an antiferromagnet, the superconducting critical temperature T_c being proportional to the magnetic moment on the lattice sites. In their study of the superconducting properties of the intermetallic compounds U_6X (X = Mn, Fe, Co, Ni) and alloys formed between these compounds Hill and Matthias[14] discuss this possibility. Although these authors do not find conclusive experimental evidence for magnetic ordering in these compounds, they nevertheless conclude that the observed correlation between the superconductivity of the U_6X compounds and the magnetic nature of the X elements very likely points to the necessity of a "noncustomary theoretical approach to superconductivity" in these compounds, i.e., the possibility of triplet pairing should be considered. Benneman and Garland[15] do not share the view that U_6X compounds are anomalous superconductors. In their view a correlation between T_c and the magnetic character of the X atoms will exist because both properties are related in a similar way to the variation of some atomic parameter η_0, which can in turn be calculated from experimental T_c values of transition metals. Engelhardt,[16] however, found experimental evidence that T_c in U_6X compounds is largely determined by the interatomic distances in the U sublattice. In view of his results and of the Mössbauer effect on ^{57}Fe in U_6Fe measured by Blow[17] he also came to the conclusion that the superconductivity in U_6X compounds is not related to the magnetic state of the X atoms. Unpublished results of Havinga[18] indicate that in U_6Fe T_c decreases sharply upon substitution of Al for Fe ($\Delta T_c \sim -1$ K/at.% Al), whereas substitutions of Gd for U up to several percent hardly affect T_c. This difference in decrease of critical temperature when adding nonmagnetic and magnetic impurities points towards the possible fulfillment of a criterion for the occurrence of triplet pairing as mentioned by BW.[4] Although BW emphasize that triplet pairing will occur in "very pure" samples only, U_6X compounds of standard purity do show properties reminiscent of spin-triplet pairing superconductivity (even according to the above quoted BW criterion concerning the influence of nonmagnetic impurities on T_c) justifying a further investigation of these materials applying our Josephson method.

Another system in which triplet pairing might be anticipated is $CeRu_2$. Theoretical arguments given by Akhiezer and Akhiezer[19] lead to this speculation. If 1-mol% $GdRu_2$ is introduced in $CeRu_2$ a slight increase of T_c is observed according to Wilhelm and Hillenbrand.[20] At higher concentrations of $GdRu_2$, mixed crystals $Ce_{1-x}Gd_xRu_2$ can be formed in which superconductivity and ferromagnetism probably coexist.[21,22] Both experimental observations fit into the Akhiezer approach to triplet-pairing superconductivity. However, for $CeRu_2$ a small increase of T_c has also been found for nonmagnetic substituents,[22] making the former experimental evidence of triplet pairing less convincing. Although no correlation is observed between T_c and the magnetic character of the X atoms in Th_7X_3 (X = Fe, Co, Ni) we nevertheless study this type of superconductor as well simply because of the occurrence of magnetic elements. For the same reason Zr_2Co and Zr_2Ni have been selected for our investigations.

IV. EXPERIMENTAL

Guided by the theoretical considerations in Sec. II we chose a simple experimental setup to search for triplet superconductivity. A sample of each of

TABLE I. Preparation, crystal structure, and critical temperature of measured samples.

Material	Reference to preparation	Crystal structure	T_c (K) observed	T_c (K) literature
U_6Fe	14	$D2_c$	3.9	3.9 [a]
Th_7Co_3	25	$D10_2$	1.84	1.83 [b]
Th_7Fe_3	25	$D10_2$	1.86	1.86 [b]
$CeRu_2$	20	$C15$	5.3	6.2 [c]
$Ce_{1-x}Gd_xRu_2$	20	$C15$	See text	
Zr_2Co	26	$C16$	5.2	5.0 [d]
Zr_2Ni	26	$C16$	1.54	1.57 [d]

[a] Reference 24. [b] Reference 25. [c] Reference 20. [d] Reference 27.

the superconductors listed in Table I is brought into contact with a sharpened Nb point. The idea is to measure I-V characteristics of this point contact below both superconducting transition temperatures as a function of microwave power directed on the point contact. The microwave-induced steps in the I-V curve can then be measured. The existence or nonexistence of the basic voltage step $h\nu/2e$ then gives an answer to the question as to whether second-order Josephson tunneling between the two superconductors exists or does not exist. In cases where difficulties would arise originating from the occurrence of subharmonics, leading to ambiguities in the determination of the "basic" step, the step length dependence on the microwave power enables us to discriminate between subharmonic and basic voltage steps.

The samples measured were prepared with well-known procedures described in the literature, starting from high-purity metal powders. X-ray analysis showed all but one of the samples to be single phase; only $CeRu_2$ contained traces of second phase, viz., Ru. Critical temperatures were determined by ac susceptibility measurements (21 Hz) as a function of temperature. The measured critical temperatures were found to agree with literature data, the only exception being $CeRu_2$, for which a somewhat lower T_c was found. Data concerning preparation and critical temperatures are given in Table I. For the $Ce_{1-x}Gd_xRu_2$ system the T_c values are not presented. In the region $0.11 < x \leq 0.13$, where the samples become superconducting and ferromagnetic at about the same temperature, a definition of T_c from susceptibility measurements becomes quite obscure. The samples can probably best be compared with those of Ref. 20 by giving the temperature at which the susceptibility reaches its maximum value. For $x = 0.11$, 0.12, and 0.13 these temperatures are 2.6, 4.0, and 4.9 K, respectively. The samples to be measured were mounted in an experimental setup in which the Nb point could be put on the surface of the sample by means of a differential micrometer screw. By careful adjustment of the screw the resistance of the point contact could be varied while the contact was at liquid-helium temperature. Microwave radiation (35 GHz) could be directed on the point contact by means of an open-ended stainless-steel waveguide. The point contact was connected with a current source and the I-V characteristics could be measured by a standard four-point technique.

In an early stage U_6Fe and $CeRu_2$ sample surfaces were prepared by polishing them. It turned out, however, that the polishing damaged the surface region in such a way that we were nearly always unable to make a superconducting contact; there remained a small but finite resistance below the critical current of the contact. The peculiarities of the I-V characteristics in such a case have been reported on earlier[28] and will briefly be commented on below in connection with Fig. 2. To avoid the difficulties with a polished surface we later used surfaces of freshly broken samples on which the Nb point was placed directly. These contacts turned out to show superconducting behavior below the critical current value with a few exceptions.

An example of such a measurement is given in Fig. 1 for a U_6Fe-Nb point contact. Due to the high critical current value of this particular case the I-V characteristic shows rather big jumps at the critical current value. With increasing microwave radiation the critical current decreases, as usual, and the jump also decreases, and we see a gradual appearance of Josephson steps at lower multiples of $h\nu/2e$. Although, especially at low microwave powers, some subharmonic steps can be seen there is no doubt that in this case the fundamental Josephson step ΔV is equal to $h\nu/2e$. For all other cases the situation was comparable as far as the subharmonic steps are concerned. The subharmonic steps were remarkably less sharp than a main Josephson step and

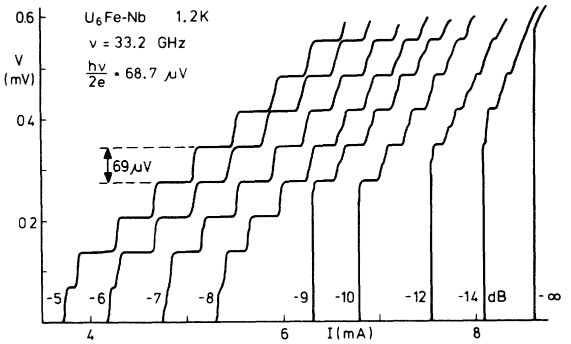

FIG. 1. I-V characteristics of a Nb-U_6Fe point contact with microwave radiation as a parameter. The dB figures along the curves are the attenuation values of the microwave radiation.

their size was usually much smaller. Moreover their microwave dependence does not fit into the Bessel-function-like dependence of the main steps on the microwave amplitude, so that in practice there was no danger of taking subharmonic steps erroneously as main steps in the experiments. The main result of the investigations is that all point contacts between a Nb point and the materials given in Table I showed an ac Josephson effect with a voltage difference ΔV between the successive steps, which agrees with second-order Josephson tunneling, that is $h\nu = 2e\Delta V$.

Figure 2 shows I-V curves for a $Ce_{0.89}Gd_{0.11}Ru_2$ sample. Although the surface of the sample is from a freshly broken piece of material, we see that the point contact remains resistive below the critical current value (where a jump in the resistance occurs). Notwithstanding this resistive behavior the contact shows an ac Josephson effect, but with a voltage difference between the steps of 32 μV, which is smaller than the value of $h\nu/2e = 68$ μV. This behavior of the point contact can be described in terms of the equivalent circuit given in Fig. 3. In series with a Josephson contact J with critical current value I_c there is a resistance R_1 while a resistance R_2 is present parallel to J and R_1. The resulting I-V curve for such a circuit can easily be calculated and is also given in Fig. 3, where J is assumed to behave as a normal Josephson junction with microwave-induced steps with a distance $\Delta V = h\nu/2e$ in its I-V curve. If one fits into this model the I-V curve without microwave radiation (see Fig. 3) one obtains $R_1 = 0.125$ Ω, $R_2 = 0.115$ Ω. This results in the reduced voltage difference $\Delta V = (h\nu/2e)[R_2/(R_1 + R_2)] = 32$ μV, which is indeed measured. This particular contact is therefore seen to behave in much the same way as point contacts between Nb and polished U_6Fe

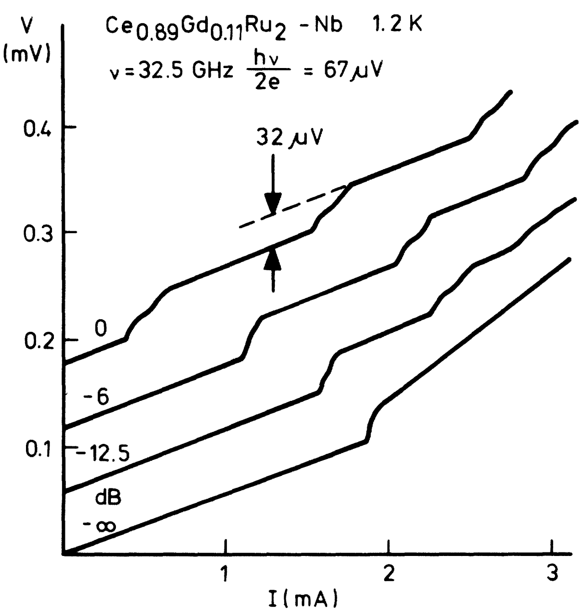

FIG. 2. I-V characteristics of a Nb-$Ce_{0.89}Gd_{0.11}Ru_2$ contact which remains resistive below the critical current value. The successive curves are shifted over 60 μV for reasons of clarity.

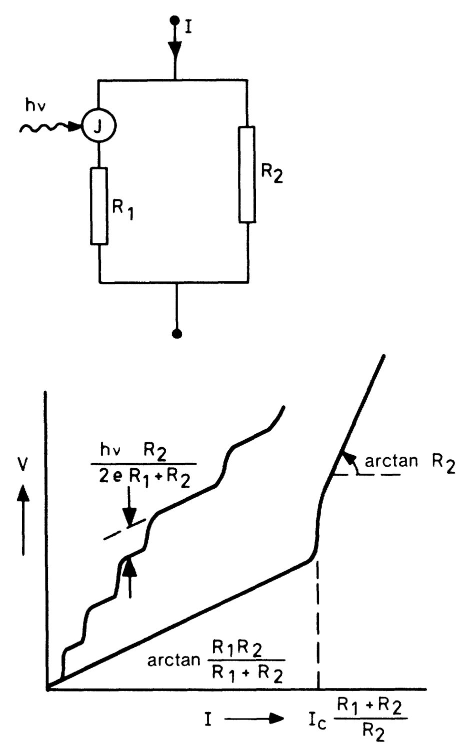

FIG. 3. Equivalent circuit of a junction that remains resistive, but still shows the ac Josephson effect with the resulting I-V characteristic.

surfaces reported on earlier.[28]

V. CONCLUSIONS

Let us recapitulate the main results of the paper. It has been shown theoretically that two weakly coupled superconductors one with pairs in a spin-singlet state the other with spin-triplet pairs will behave, as far as the Josephson effect is concerned, quite differently under quite general conditions compared with two weakly coupled singlet-pairing superconductors. Owing to different symmetry properties of the wave functions of the singlet- and the triplet-pairing superconductor the normal Josephson effects connected with second-order tunneling are shown to be absent in the case where the coupling can be described by a spin-conserving tunnel Hamiltonian. This conclusion is also shown to be correct in the case that spin flip of the tunneling electrons may occur due to exchange with paramagnetic impurities in the barrier. Josephson effects may exist in fourth order of the transition matrix elements, but these lead to the phase difference relation $d\phi/dt = 4eV/\hbar$. This offers the possibility of investigating whether a particular superconductor has spin triplet-pairs by coupling it weakly to a superconductor believed to be in a spin-singlet-pairing state. The criterion for deciding whether the two coupled superconductors are in the same state or not is the existence or nonexistence of the ac Josephson effect with $\Delta V = h\nu/2e$.

If for some contact between two superconductors a Josephson effect would arise with $\Delta V = h\nu/4e$ and not with $\Delta V = h\nu/2e$ it is certain that one of the superconductors is in a pure singlet state, the other in a pure triplet state. In all cases where an ac Josephson effect is observed with $\Delta V = h\nu/2e$ we have proven under quite general conditions that both superconductors are in the same spin state. In the physically unlikely situation that one of the superconductors should be in a mixed spin state the occurrence of the relation $\Delta V = h\nu/2e$ does not give an unambiguous answer as to whether both superconductors are in the same spin state. It should furthermore be emphasized that in the case of magnetic impurities in the barrier the above criterion is proven to be valid for randomly oriented magnetic moments of these impurities.

Several materials for which spin-triplet pairing has been suggested have been investigated. After weakly coupling them to Nb by making a point-contact junction, we looked for the ac Josephson effect. All materials investigated showed a Josephson effect with the Nb point with $\Delta V = h\nu/2e$. The conclusion is therefore that these experiments give strong evidence that these materials are not in a state with spin-triplet pairing, but in the normal spin-singlet state, which is thought to be the state of niobium.

Furthermore, it turns out to be questionable whether a large depression of T_c by nonmagnetic impurities *and* the occurrence of triplet superconductivity are related as stated by Balian and Werthamer.[4] Although a large depression of T_c was observed in U_6Fe, due to the introduction of nonmagnetic aluminum impurities, no triplet superconductivity was found in nonintentionally doped samples of U_6Fe applying the Josephson criterion.

Whether or not these or other materials might become triplet superconductors if much purer samples will become available–according to BW, triplet superconductivity is only possible in "very pure" materials—remains disputable. Our conclusion regarding the nonexistence of triplet superconductors refers to real materials, mentioned in the literature, and defined by their T_c and crystallographic data.

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APPENDIX

In Sec. II it has been proven that no Josephson effect up to second order in the tunnel-matrix elements exists if the two coupled superconductors are in a different pure spin state. The derivation is based on the spin-conserving character of the tunnel Hamiltonian H_T of Eq. (1). It is doubtful whether this special form of tunnel Hamiltonian applies especially if one of the two superconductors contains magnetic elements, as is often the case (Table I). Some of these magnetic atoms may easily get incorporated in the tunnel barrier where they form magnetic impurities which may cause spin flip of the tunneling electrons. We therefore investigate a more general Hamiltonian which describes not only the interaction between the coupled superconductors, but also the interaction with localized but mutually uncoupled paramagnetic impurities.

Such a Hamiltonian has been presented by Appelbaum[29,30]

$$H_i = H_T + H_J + H_{TJ} . \tag{7}$$

H_T is the normal tunnel Hamiltonian of Eq. (1). H_J is the Hamiltonian describing the interaction of superconductor 1 with a paramagnetic impurity

$$H_J = J \sum_{\vec{k}_1 \vec{k}_1'} [S_z(a^\dagger_{\vec{k}_1\uparrow} a_{\vec{k}_1'\uparrow} - a^\dagger_{\vec{k}_1\downarrow} a_{\vec{k}_1'\downarrow}) + S^+ a^\dagger_{\vec{k}_1\downarrow} a_{\vec{k}_1'\uparrow} + S^- a^\dagger_{\vec{k}_1\uparrow} a_{\vec{k}_1'\downarrow}] . \tag{8}$$

We assume the impurities to be localized on the side of superconductor 1 in the barrier, and we therefore neglect the equivalent interaction term with superconductor 2, although this term can easily be incorporated without altering the conclusions of this appendix. The Hamiltonian H_{TJ} describes tunneling of electrons through the barrier via interaction with the impurity

$$H_{TJ}=T_J\sum_{\vec{k}_1\vec{k}_2}[S_z(a^\dagger_{\vec{k}_1\uparrow}a_{\vec{k}_2\uparrow}+a^\dagger_{\vec{k}_2\uparrow}a_{\vec{k}_1\uparrow})-S_z(a^\dagger_{\vec{k}_1\downarrow}a_{\vec{k}_2\downarrow}+a^\dagger_{\vec{k}_2\downarrow}a_{\vec{k}_1\downarrow})+S^+(a^\dagger_{\vec{k}_1\downarrow}a_{\vec{k}_2\uparrow}+a^\dagger_{\vec{k}_2\downarrow}a_{\vec{k}_1\uparrow})+S^-(a^\dagger_{\vec{k}_1\uparrow}a_{\vec{k}_2\downarrow}+a^\dagger_{\vec{k}_2\uparrow}a_{\vec{k}_1\downarrow})]\,. \tag{9}$$

In these equations S_z, S^+, and S^- are the standard spin operators working on the paramagnetic impurity. We have also assumed J and T_J to be real and independent of $\vec{k}_1$ and $\vec{k}_2$. It can easily be shown, however, that this assumption is not essential; all conclusions hold for general matrix elements $J_{\vec{k}_1\vec{k}_1'}$ and $T_{J\vec{k}_1\vec{k}_2}$ as well.

The perturbation calculation for the current $I(t)$ between the two superconductors leads to the following expression in first order of the perturbing Hamiltonian H_i:

$$I(t)=\frac{i}{\hbar}\int_{-\infty}^{t}e^{\eta t'}dt'\langle[H_i(t'),I_T(t)+I_{TJ}(t)]\rangle\,, \tag{10}$$

where $\eta\to+0$ and where the brackets [ ] stand for a commutator and $\langle\ \rangle$ for a thermal average over the states of the unperturbed Hamiltonian of the system containing both superconductors and the paramagnetic impurity. In this general case the current operator is seen to consist of two parts, the first part originating from H_T, the second from H_{TJ}:

$$I_T=\frac{e}{i\hbar}\sum_{\vec{k}_1\vec{k}_2}[T_{\vec{k}_1\vec{k}_2}(a^\dagger_{\vec{k}_1\uparrow}a_{\vec{k}_2\uparrow}+a^\dagger_{\vec{k}_1\downarrow}a_{\vec{k}_2\downarrow})-T^*_{\vec{k}_1\vec{k}_2}(a^\dagger_{\vec{k}_2\uparrow}a_{\vec{k}_1\uparrow}+a^\dagger_{\vec{k}_2\downarrow}a_{\vec{k}_1\downarrow})]\,, \tag{11}$$

$$I_{TJ}=\frac{e}{i\hbar}\sum_{\vec{k}_1\vec{k}_2}T_J[S_z(a^\dagger_{\vec{k}_1\uparrow}a_{\vec{k}_2\uparrow}-a^\dagger_{\vec{k}_2\uparrow}a_{\vec{k}_1\uparrow})-S_z(a^\dagger_{\vec{k}_1\downarrow}a_{\vec{k}_2\downarrow}-a^\dagger_{\vec{k}_2\downarrow}a_{\vec{k}_1\downarrow})+S^+(a^\dagger_{\vec{k}_1\downarrow}a_{\vec{k}_2\uparrow}-a^\dagger_{\vec{k}_2\downarrow}a_{\vec{k}_1\uparrow})+S^-(a^\dagger_{\vec{k}_1\uparrow}a_{\vec{k}_2\downarrow}-a^\dagger_{\vec{k}_2\uparrow}a_{\vec{k}_1\downarrow})]\,. \tag{12}$$

We have already shown in Sec. II that for coupling between a triplet superconductor 1 and a singlet superconductor 2 the following relation holds:

$$\langle[H_T(t'),I_T(t)]\rangle_{\text{ph}}=0\,, \tag{13}$$

where the subscript ph means that only the phase-dependent parts of the expectation value are considered. One also has

$$\langle[H_T(t'),I_{TJ}(t)]\rangle=\langle[H_{TJ}(t'),I_T(t)]\rangle=0 \tag{14}$$

because of the fact that both commutators contain only one spin operator acting on the impurity. For randomly oriented paramagnetic impurities the expectation value of a single spin operator is zero,

$$\langle S_z\rangle=\langle S^+\rangle=\langle S^-\rangle=0\,. \tag{15}$$

If, due to interactions, the impurity has no longer a randomly oriented spin, $\langle S_z\rangle$ may be unequal to zero and Eq. (14) then does not hold for this situation. The term in the expectation value of Eq. (10) arising from H_J is zero because its commutator with I_T or I_{TJ} contains three annihilation or creation operators of superconductor 1 and only one of superconductor 2.

The only remaining possible phase-dependent contribution to Eq. (10) originates from the expectation value of the commutator of H_{TJ} and I_{TJ}; this commutator contains the nonzero spin expectation values $\langle S_z^2\rangle$, $\langle S^+S^-\rangle$, and $\langle S^-S^+\rangle$. A typical term in this commutator is, for instance,

$$T_J^2\langle S_z a^\dagger_{\vec{k}_1\uparrow}(t')a_{\vec{k}_2\uparrow}(t')(-S_z)a^\dagger_{-\vec{k}_1\downarrow}(t)a_{-\vec{k}_2\downarrow}(t)\rangle=T_J^2\langle S_z^2\rangle\langle a^\dagger_{\vec{k}_1\uparrow}(t')a^\dagger_{-\vec{k}_1\downarrow}(t)\rangle\langle a_{\vec{k}_2\uparrow}(t')a_{-\vec{k}_2\downarrow}(t)\rangle\,. \tag{16}$$

However, due to relations (4) this term cancels the term with reversed $\vec{k}_1$ and $\vec{k}_2$ vectors, in the same way as the terms in expression (3) did. The same reasoning holds for all other contributions to the commutator of H_{TJ} and I_{TJ}. It is therefore concluded that phase-dependent contributions to Eq. (10) are identically equal to zero.

The terms in Eq. (10) are of second order in the matrix elements $T_{\vec{k}_1\vec{k}_2}$ and or T_J. There are of course contributions to the current expression which are of higher-order in the Hamiltonian H_i, but still of second order in the matrix elements T the reason being the term H_J. These higher order contributions may very well be significant as $|J|$ can be large compared to $|T_J|$ or $|T_{\vec{k}_1\vec{k}_2}|$. Take for instance a contribution to the current that is third order in H_t but still of second order in T:

$$-\frac{e}{\hbar^2}\int_{-\infty}^{t}dt'\int_{-\infty}^{t'}dt''\, e^{\eta(t'+t'')}\langle I_T(t)H_J(t')H_{TJ}(t'')\rangle, \tag{17}$$

in which $\eta\to+0$. The threefold product of operators in Eq. (17) contains products of two spin operators, the expectation values of which are nonzero. A careful analysis reveals that the expectation value in Eq. (17) contains the following sum

$$\sum_{\vec{k}_1\vec{k}_2\vec{k}_1'} T_{\vec{k}_1\vec{k}_2}T_J J\{\langle S^+S^-\rangle[\langle a^\dagger_{\vec{k}_1'\downarrow}(t')a^\dagger_{-\vec{k}_1'\uparrow}(t'')\rangle\langle a^\dagger_{\vec{k}_1\uparrow}(t)a_{\vec{k}_1\uparrow}(t')\rangle-\langle a^\dagger_{\vec{k}_1\uparrow}(t)a^\dagger_{-\vec{k}_1\downarrow}(t')\rangle\langle a_{\vec{k}_1'\uparrow}(t')a^\dagger_{\vec{k}_1'\uparrow}(t'')\rangle]\langle a_{\vec{k}_2\uparrow}(t)a_{-\vec{k}_2\downarrow}(t'')\rangle$$
$$+\langle S^-S^+\rangle[\langle a^\dagger_{\vec{k}_1'\uparrow}(t')a^\dagger_{-\vec{k}_1'\downarrow}(t'')\rangle\langle a^\dagger_{\vec{k}_1\downarrow}(t)a_{\vec{k}_1\downarrow}(t')\rangle-\langle a^\dagger_{\vec{k}_1\downarrow}(t)a^\dagger_{-\vec{k}_1\uparrow}(t')\rangle\langle a_{\vec{k}_1'\downarrow}(t')a^\dagger_{\vec{k}_1'\downarrow}(t'')\rangle]\langle a_{\vec{k}_2\downarrow}(t)a_{-\vec{k}_2\uparrow}(t'')\rangle\}. \tag{18}$$

This sum can be seen to be equal to zero by using relations (4) and by realizing that

$$\langle S^+S^-\rangle=\langle S^-S^+\rangle$$

and

$$\langle a^\dagger_{\vec{k}_1\uparrow}a_{\vec{k}_1\uparrow}\rangle=\langle a^\dagger_{\vec{k}_1\downarrow}a_{\vec{k}_1\downarrow}\rangle.$$

Similar arguments hold for any higher-order contribution containing only two matrix elements T_J or $T_{\vec{k}_1\vec{k}_2}$. The conclusion is therefore that the presence of paramagnetic impurities with randomly oriented moments with which the tunneling electrons may exchange spins does not open an extra channel for phase-dependent Josephson tunneling. In arriving at this conclusion we have used the fact that the expectation value of the z component of spin of the paramagnetic impurity is zero. In the situation that this condition is not fulfilled, because of mutual interaction of the impurities or because of interaction of the impurity with the triplet superconductor, the conclusion that there is no second-order Josephson effect between a triplet and singlet superconductor is not justified.

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