In the case of the usual coupling parameters, with

$$U_N(\vec{N};\vec{\xi}_N)=\sum_{i,j\subset\vec{N}}\xi_i\xi_jU_{ij},$$

it can be shown that $G_n(\vec{n};\vec{\xi}_n)$ can be written in a form similar to Eq. (8) with $\lambda_i\lambda_jf_{1j}$ replaced by $f_{1j}(\xi_1,\xi_j)=\exp(-\xi_1\xi_jU_{ij}/kT)-1$ and with the corresponding adjustment for the Boltzmann factors. The convergence of these expansions is proved by the same arguments as for Eq. (8). Such expansions, however, are not Taylor expansions of $G_n(\vec{n};\vec{\xi}_n)$ in ξ_1 but, rather, resummations of these expansions into convergent forms.

The present proof cannot be applied to the customary distribution functions $g_n(\vec{n};\vec{\lambda}_n)$. The most that can be said about convergence of an expansion of $g_n(\vec{n};\vec{\lambda}_n)$ in powers of λ_i, $i\subset\vec{n}$, is that g_n can be expressed as a ratio of two converging series.

The functions $G_n(\vec{n})$ yield the usual thermodynamic functions (with activity instead of density as independent variable) through the same theorems as for $g_n(\vec{n})$.

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[1]See, e.g., J. G. Kirkwood and J. C. Poirier, J. Phys. Chem. 58, 591 (1964), and references cited therein.

[2]E. Meeron, Phys. Rev. 126, 883 (1962).

[3]Strictly speaking, z_j in Eq. (3) equals thermodynamic activity only after taking the thermodynamic limit on the left-hand side.

[4]The dependence of $\alpha(\lambda_1)$ on any finite number of coupling parameters from among the N-1 remaining ones is thermodynamically negligible. The same situation obtains for distribution functions: $g_n(\vec{n};\vec{\lambda}_n)$ depends strongly only on the $\vec{n}$ coupling parameters of the set $\vec{n}$ [see J. G. Kirkwood, J. Chem. Phys. 3, 300 (1935)].

[5]Kirkwood, Ref. 4.

[6]In order to obtain Eq. (7), the coupling parameters of the set $\vec{N}$-$\vec{n}$ were all set equal to λ_j, and terms $O(n/V)$ ($\rightarrow 0$ in thermodynamic limit) neglected. Retaining a different value for each coupling parameter merely results in a very cumbersome notation but does not affect our proofs.

[7]In the case of Coulombic potentials with short-range repulsion, $f_0=\infty$, but the expansion can be resummed so that the Debye potential replaces the Coulombic potential. The corresponding integrals are then finite.

[8]J. G. Kirkwood and Z. Salzburg, Discussions Faraday Soc. 15, 28 (1953).

DIRECT OBSERVATION OF ELECTRON-PAIRING EFFECT IN TYPE-II SUPERCONDUCTORS BY POSITRON ANNIHILATION

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We have performed angular-distribution measurements of the two gammas produced by annihilation of positrons in a type-II superconductor (Nb_3Sn) to detect the superconducting smearing effect on the electrons momentum distribution function. Our results give, for the first time, a direct experimental evidence of the redistribution of K-space states at the superconducting transition.

In a normal metal the electron distribution function is the Fermi-Dirac one, but, for the superconducting state, the BCS theory predicts a redistribution in K space, because of the electron pairing.[1,2] Although there are, at present, many experimental proofs of this theory, it has been impossible, until now, to obtain a direct observation of the modified distribution in K space. The positron annihilation technique allows the measurement of the electron momentum[3,4]; we have used it on a sample of Nb_3Sn to show the superconducting smearing effect on the electrons' momentum distribution function.

At absolute zero, the smearing range δK of the momentum distribution function in a superconductor is given by[1]

$$\delta K=\Delta/hV_F\simeq 1/\xi,\tag{1}$$

where Δ is the superconducting energy gap, V_F is the Fermi velocity, and ξ is the coherence length. In a type-I superconductor ξ is typically

10^3-10^4 Å, so that $\delta K/K_F \simeq 10^{-3}$-$10^{-4}$.

The attainable angular resolution in a positron annihilation experiment corresponds to about $\delta K \simeq 0.1 K_F$, and clearly it does not allow the detection of any smearing effect in type-I superconductors. In fact, measurements carried out by Briscoe, Beardsley, and Stewart[5] by means of positron annihilation, at 10 and 4.2°K in a Pb single crystal, gave negative results.

On the contrary, some type-II superconductors have a very small coherence length, $\xi \simeq 50$ Å, corresponding to a $\delta K \simeq 10^{-1} K_F$, well observable with positron technique. Among type-II superconductors we selected Nb_3Sn because of its small coherence length and high transition temperature, $T_c \simeq 18$°K[6]; the last property allows us to work at a temperature of 4.2°K, where δK is very near to its maximum.

The thermal smearing of the Fermi-Dirac distribution is neglibibly small, even at room temperature ($\delta K \simeq 10^{-2} K_F$); unfortunately we cannot assume a vanishingly small momentum distribution for positrons.[7-9] In fact, if we suppose that the positron is thermalized before the annihilation, its contribution to the total momentum, near K_F, at $T = 300$°K, is $K_+ \simeq 10^{-1} K_F$, and this is observable as we outlined before. However, Kim, Stewart, and Carbotte,[8] at least for the alkali metals, have proved that below a certain temperature the positrons retain a minimum constant energy. We will keep in mind this point when discussing our results below.

Our experimental apparatus is a conventional one in positron-annihilation measurements and it is described in detail elsewhere.[10] The sample is a Nb_3Sn polycrystal, in the form of a hollow cylinder, within which was introduced a source of Na^{22}, 1 mCi of activity. The detector slits subtended at the specimen an angle of 0.65 mrad and the position of the moving slit was measured with a precision better than 0.05 mrad; it is possible to neglect any correction due to the finite length of the slits, since they subtend an angle of ±30 mrad.

With such an apparatus we performed careful angular distribution measurements of the two-γ annihilations at three different temperatures: 300, 80, and 4.2°K. The results, corrected for the absorption of the cooling liquids and after subtraction of the background, are shown in Fig. 1. The full-line curves result from a best fit of the experimental points obtained by a computer and they fit quite well the experimental points. The errors, sometimes smaller than the physical dimensions of the points, are the statistical ones. There is evident a small shift of the curve obtained at 4.2°K with respect to the other two curves, due to some thermal contraction, which can be measured with great accuracy. In the same figure is shown the Gaussian curve, obtained by a best fit of the tail of the angular distributions, in order to take into account the contributions of core electrons.[11] It is evident that neither the height of the curves nor their area changes as the temperature decreases, in good agreement with recent measurements.[10] At $\theta = \theta_F$ only the angular correlation curve performed at $T = 80$°K shows a quite sharp knee, which really would be smoother, taking into account the resolution; in contrast at this value of θ the curves measured at $T = 300$ and 4.2°K are smooth. With the help of a computer, from the measured data we obtained the following figures for the half-height width (hhw) and the Fermi angle θ_F:

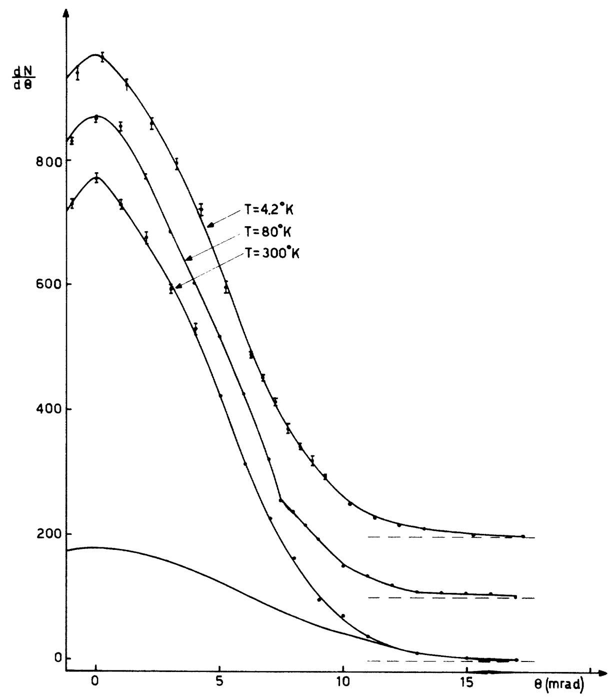

FIG. 1. Angular correlation of photons from positrons annihilating in niobium stannide at the temperatures indicated.

$$\mathrm{hhw}_{300} = 10.7 \pm 0.1 \text{ mrad},$$

$$\mathrm{hhw}_{80} = 10.7 \pm 0.1 \text{ mrad},$$

$$\mathrm{hhw}_{4.2} = 10.8 \pm 0.1 \text{ mrad},$$

$$\theta_F = 7.5 \pm 0.1 \text{ mrad}.$$

We will now discuss our results, bearing in mind the conclusions of previous works[7-9] on the minimum energy of positrons at low temperatures; only this effect could mask the superconducting smearing. In order to clarify the situation, we will examine the following possible cases: (i) First of all we shall consider what should be the result of an angular correlation measurement, assuming only a contribution from thermalized positrons; in this case, as the temperature decreases, a corresponding decrease of the smearing due to the reduced thermal motion of positrons will be observed. (ii) Supposing, conversely, that below a certain temperature the positrons retain a minimum energy, the smearing will be kept constant. (iii) If the positrons are thermalized and a strong superconducting smearing is present, at $T=4.2°K$ the only contribution will arise from superconductivity. (iv) The worst case is the coexistence of the positron minimum energy and superconducting smearing; in such a case the smearing effect due to the superconductivity is observable only if it is of the same order of magnitude as that arising from the positron motion.

Consequently the most convincing test of the smearing effect due to the superconductivity is a comparison between the results in the normal and superconducting state. Hence it is clear that any observed increase of the smearing in the curves at lowest temperature cannot be due to the motion of positrons.

Now we can analyze in detail our results: A comparison between the curves at $T=300$ and $T=80°K$ allows us to say that there is evident a clear decrease of positron residual energy (the smearing is very much reduced at 80°K). Although we do not know if at $T=80°K$ the positrons are thermalized, the comparison between the curves at $T=80$ and $T=4.2°K$ furnishes, as we outlined before, experimental evidence of the observability of the superconducting smearing. (See the difference curve in Fig. 2.) If we suppose the positrons thermalized at all temperatures, the difference in smearing between 80 and 4.2°K curves gives directly a measure of the coherence length of our sample; if this is not the case, it would be necessary to determine exactly the minimum energy of positrons.

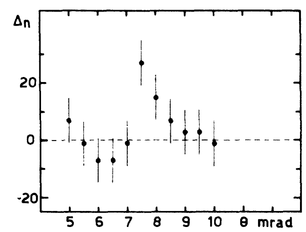

FIG. 2. Plot of differences between experimental curves at $T=4.2$ and $T=80°K$, near θ_F, showing the observed smearing effect due to superconductivity.

We believe that in any case our measurements have a conceptual value, because they give a direct experimental evidence of the redistribution of K-space states, predicted by BCS theory. However we do not think this technique is convenient for quantitative measurements, which can be obtained indirectly in other ways, with greater accuracy.

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