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\*Work supported by the U. S. Air Force under Contract No. AF33(615)-1915.

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### BOUNDARY SCATTERING IN SUPERCONDUCTORS\*

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(Received 1 December 1967)

Boundary scattering in gallium single crystals produces little shift of the superconducting critical temperature  $T_c$  consistent with the assumption of specular reflection of quasiparticles at the sample boundary.

This paper reports the results of an investigation of the effect on  $T_c$  of reducing the mean free path (mfp) in 99.9999% pure gallium single crystals by means of boundary scattering. The purpose of this investigation was to observe the so-called "mfp" effect first noted by Lynton, Serin, and Zucker.<sup>1</sup> This effect, a consistently observed reduction of  $T_c$  with reduction of mfp by the addition of impurities, was explained theoretically as the result of averaging the anisotropic pairing interaction present in real superconductors.<sup>2</sup>

21 single-crystal plates of gallium with thickness ranging from 25 to 250  $\mu$  were used in this investigation. The crystals were divided into three approximately equal groups with the crystals of each group having one of the principal axes of gallium perpendicular to the surface of the thin plate. Shifts in critical temperature were measured in reference to bulk single crystals of identical purity using the change in mutual inductance of a pair of coils containing the sample as an indication of the phase transition. Previous experiments<sup>3</sup> had shown that the critical temperatures of the plates could be determined to at least  $\pm 10^{-4}$  °K using this technique. Further details of the experimental procedure and sample making are given in Ref. 3.

The experimental results are shown in Fig. 1, where the shift in  $T_c$  of the thin plates from the  $T_c$  of bulk gallium samples is plotted versus  $1/d$ , where  $d$  is the sample thickness. One can see that for samples of all orientations, the shift in  $T_c$  is negligible. The data gave the best least-squares fit to a function of the form  $\Delta T_c = A/d + B$  and it was found that  $A = (-0.28 \pm 0.059) \times 10^{-6}$  °K cm and  $B = (0.10 \pm 0.04) \times 10^{-3}$  °K. The constant term  $B$  is of the order of the scatter in the data and only represents the slight uncertainty in the measurement of  $T_c$ . Associating the  $A$  term with the mfp effect, we find that this shift of  $T_c$  with specimen thickness, when converted to  $\Delta T_c$  versus mfp,<sup>4</sup> is much smaller than that reported earlier for the mfp effect.<sup>1,2</sup> In fact, the shift of  $T_c$  may be zero within the uncertainty of the data. This apparent lack of a mfp effect is surprising since the Fermi velocity of gallium is typically<sup>5</sup>  $6 \times 10^7$  cm/sec, so that scattering from the boundaries of a film 25  $\mu$  thick will take place every  $5 \times 10^{-11}$  sec. The lifetime of superconducting pairs has been calculated<sup>6</sup> and measured<sup>7</sup> to be of the order of  $4 \times 10^{-8}$  sec; hence many thousand collisions should occur during the typical pair lifetime and anisotropy averaging should be complete.

When the results shown in Fig. 1 were found,

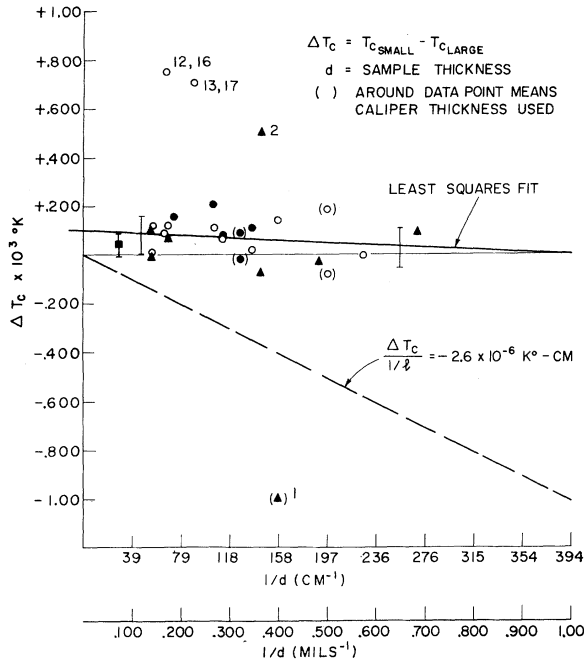


FIG. 1. The shift of  $T_c$  with specimen thickness in single-crystal gallium plates. Open triangles, A-axis samples; open circles, B-axis samples; solid circles, C-axis samples.  $\Delta T_c/(1/l)$  is computed for  $\lambda=1$  and  $l=d$  [see Eq. (3)]. Numbered points correspond to data from damaged samples and were excluded from the analysis.

the effect of boundary scattering on another superconductor was investigated. 5- $\mu$  thick pounded and annealed indium foils were found to exhibit the same mfp effect as indium with impurities added.<sup>9</sup> This same result was obtained earlier by Lynton and McLachlan<sup>9</sup> using similar foils. However, in both this investigation and in Ref. 9 the superconducting transition widths were considerably broadened compared with the gallium data, presumably because of the less desirable metallurgical condition of the indium samples. Preliminary data obtained by this author and C. A. Shiffman indicate that gallium with silver impurity added exhibits a shift of  $T_c$  comparable with that found in other metals with the impurity-addition technique for limiting the mfp.

The boundary-scattering results for gallium just quoted can be shown to be consistent with the anisotropy-averaging interpretation of the mfp effect when specular reflection occurs at the boundary of the sample. The starting point will be the Markowitz-Kadanoff<sup>2</sup> theory for the mfp effect. These authors assume that the an-

isotropic pairing interaction can be written in the separable form

$$V_{pp'} = [1 + a(\hat{\Omega})]V[1 + a(\hat{\Omega}')], \quad (1)$$

where  $\hat{\Omega}$  and  $\hat{\Omega}'$  are unit vectors in the direction of the quasiparticle momenta  $p$  and  $p'$ . This approach concentrates the anisotropy in the angular factor  $a(\hat{\Omega})$  which is defined such that

$$\int a(\hat{\Omega})(d\Omega/4\pi) = 0; \quad \int a^2(\hat{\Omega})(d\Omega/4\pi) = \langle a^2 \rangle \neq 0. \quad (2)$$

The lowest order correction to  $T_c$  for anisotropy averaging is, therefore, proportional to the mean-square anisotropy factor  $\langle a^2 \rangle$  and is given by

$$\frac{\Delta T_c}{T_c} = -0.36 \langle a^2 \rangle \frac{\pi \epsilon(0) \xi_0}{2 k T_c l} \lambda. \quad (3)$$

In Eq. (3),  $l$  is the electronic mfp,  $\epsilon(0)$  the 0°K energy gap, and  $\xi_0$  the coherence length. Our ignorance of the details of the scattering process is contained in the parameter  $\lambda$ . This factor is the ratio of the collision integral for anisotropy averaging to that for transport processes, i.e., a ratio of the collision time  $\tau_{\text{coll}}$  to the characteristic time to remove anisotropy  $\tau_{\text{an}}$ :

$$\lambda = \frac{\tau_{\text{coll}}}{\tau_{\text{an}}} = \frac{\int \frac{d\Omega}{4\pi} \int d\Omega' \frac{d\sigma(\hat{\Omega} \rightarrow \hat{\Omega}')}{d\Omega'} \left[ 1 - \frac{a(\hat{\Omega})a(\hat{\Omega}')}{\langle a^2 \rangle} \right]}{\int \frac{d\Omega}{4\pi} \int d\Omega' \frac{d\sigma(\hat{\Omega} \rightarrow \hat{\Omega}')}{d\Omega'} [1 - \hat{\Omega} \cdot \hat{\Omega}']}, \quad (4)$$

where  $\hat{\Omega}$  = incoming direction and  $\hat{\Omega}'$  = scattered out direction. The  $\lambda$  factor was not computed by Markowitz and Kadanoff because the anisotropy  $a(\hat{\Omega})$  and the differential cross section for impurity scattering  $d\sigma/d\Omega$  were not known. For impurity scattering  $d\sigma/d\Omega$  would indeed be difficult to obtain, but  $d\sigma/d\Omega$  for scattering from two parallel boundaries is of a simple form and can be readily estimated. This was done by comparing a calculation of the average collision distance between two thin plates, made by actually averaging the distances between collisions, with the same calculation made assuming a cross section, i.e.,

$$\langle l^{-1} \rangle = \tau_{\text{coll}}^{-1} V_F^{-1}, \quad (5)$$

where  $V_F$  = Fermi velocity and  $\tau_{\text{coll}}$  is proportional to the denominator in Eq. (4) except that the back-scattering factor  $(1 - \hat{\Omega} \cdot \hat{\Omega}')$  is not used

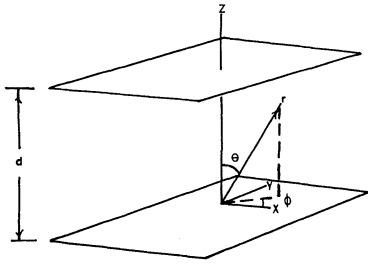


FIG. 2. Coordinate system used for boundary scattering calculations.

since no account can be taken of this in calculating  $\langle l^{-1} \rangle_{\text{av}}$  directly. The coordinate chosen for calculating  $\langle l^{-1} \rangle_{\text{av}}$  is illustrated in Fig. 2. Care was taken to include the possibility of scattering from bulk impurities by weighting the travel distance  $r$  of a quasiparticle by the Chambers factor  $\exp(-r/l_0)$ , where  $l_0$  is the mfp in bulk pure material. We then took  $\langle l^{-1} \rangle \equiv \langle \langle l \rangle_z^{-1} \rangle_{\theta, \varphi}$  and found that

$$\frac{d\sigma}{d\Omega} \propto \left\{ 1 - \frac{l_0}{d} |\cos\theta| \left[ 1 - \exp\left(-\frac{d}{l_0 |\cos\theta|}\right) \right] \right\}^{-1}. \quad (6)$$

For both our gallium and indium films  $l_0/d \approx 80$ , and for large values of  $l_0/d$  like this one can show that Eq. (6) is equivalent to better than

1% for all angles  $\theta$  to

$$(2l_0/d - 1) |\cos\theta| + 1. \quad (7)$$

Some information must be added about the type of scattering that occurs in order to find the dependence of  $d\sigma/d\Omega$  on the scattering-out solid angle  $\Omega'$ . The two easiest assumptions are diffuse scattering, where  $d\sigma/d\Omega$  is not a function of  $\Omega'$ , and specular scattering, where  $\theta' = \pi - \theta$  and  $\varphi' = \varphi$ . In addition, we do not expect scattering to result in quasiparticles appearing outside the thin plate; so we must restrict  $\theta'$  to the range  $-\frac{1}{2}\pi$  to  $\frac{3}{2}\pi$  for  $\theta$  in the range  $-\frac{1}{2}\pi$  to  $+\frac{1}{2}\pi$  and  $\theta'$  to the range  $-\frac{1}{2}\pi$  to  $+\frac{1}{2}\pi$  for  $\theta$  in the range  $\frac{1}{2}\pi$  to  $+\frac{3}{2}\pi$ . We then can combine Eqs. (7) and (4) and compute  $\tau$  for various cases of diffuse and specular reflection in the normal ( $\tau_{\text{coll}}$ ) and superconducting ( $\tau_{\text{an}}$ ) states. Three cases will be considered:

$$\lambda_1 = \frac{(\tau_{\text{coll}})_{\text{diffuse}}}{(\tau_{\text{an}})_{\text{diffuse}}}, \quad \lambda_2 = \frac{(\tau_{\text{coll}})_{\text{diffuse}}}{(\tau_{\text{an}})_{\text{specular}}},$$

$$\lambda_3 = \frac{(\tau_{\text{coll}})_{\text{specular}}}{(\tau_{\text{an}})_{\text{specular}}}.$$

We must now know something about  $a(\hat{\Omega})$  in order to proceed. Assume that an angular dependence of the form

$$a(\hat{\Omega}) = a(\theta, \varphi) = \sum_{n, m, p, q} (B_m \sin m\theta + C_n \cos n\theta)(D_p \sin p\varphi + E_q \cos q\varphi) \quad (8)$$

will be sufficient to describe  $a(\hat{\Omega})$ . One may then show the following for  $l_0/d = 80$ : (1)  $\lambda_1, \lambda_2, \lambda_3$  are not strongly affected by the  $\varphi$  dependence of  $a(\hat{\Omega})$ ; (2)  $\lambda_1$  is also insensitive to the  $\theta$  dependence of  $a(\hat{\Omega})$ ; (3) the minimum value of  $\lambda_1$  is 0.75, while the minimum value of  $\lambda_3$  is 0.3 and the maximum value of  $\lambda_2$  is 0.2, and these extrema occur only for the simple case of  $a(\hat{\Omega}) \propto \sin 2\theta$ ; (4) the relative values of  $B_m, C_n, D_p,$  and  $E_q$  are not important but tend only to mix the extreme cases using pure cosine or pure sine dependence for  $\theta$  and  $\varphi$ . These conclusions were reached by applying the conditions of Eq. (2) to Eq. (8) and computing  $\lambda_1, \lambda_2,$  and  $\lambda_3$  for all permutations of  $m, n, p, q \leq 6$  using a computer. A careful inspection will show that all of those results are to be expected from the physical model of  $\Delta T_C$  being due to anisotropy averaging. For example, for  $\lambda_2$  we expect  $\lambda \approx 0$  if  $a(\theta, \varphi) = a(\pi - \theta, \varphi)$  since

no anisotropy has been averaged out. For  $a(\theta, \varphi)$  functions with this symmetry, one finds  $\lambda_2 = 0.02 - 0.004$ , where the residual shift of  $T_C$  could be due to the bulk scattering taken into account with the factor  $e^{-r/l_0}$ . Since the results are to be applied to gallium and indium, one could inject more specific assumptions about the symmetry of these lattices to limit the values chosen of  $n, m, p,$  and  $q$  and about the ratio of anisotropy of various parameters of those metals from one axis to another to limit the choices of  $B_m, C_n, D_p,$  and  $E_q$ . This was done but was not needed since the result (3) was always obtained.

Returning to Fig. 1, we note that the experimental data for gallium correspond to  $\lambda = 0.23 \pm 0.05$  for all sample orientations when appropriate values of the parameters needed are inserted into Eq. (3)<sup>10</sup> and the appropriate val-

ue of  $l$  is used.<sup>4</sup> Thus gallium clearly falls into the category of specular reflection in the superconducting state, while indium<sup>8</sup> with  $\lambda = 0.5 \pm 0.1$  is an in-between case. Gallium has already been found to agree with the assumption of diffuse reflection for normal-state dc conductivity.<sup>11</sup>

Thus it appears that the boundary scattering in gallium changes from diffuse to specular as the sample goes from normal to superconducting. One may ask what property of the superconducting state encourages this. One possibility is that the pairing correlation produces this result. For example, it is reasonable that a surface which looked rough to a single quasiparticle with a de Broglie wavelength of a few angstroms<sup>11</sup> might look smooth to a pair that has a wave function with a spatial extent on the order of  $\xi_0$  ( $\xi_0 \cong 10^4 \text{ \AA}$ ). The situation with indium could be the result of poorer metallurgical condition of the specimens producing shifts of  $T_c$  unrelated to the mfp effect, or it could be that the indium polycrystals produce significant anisotropy averaging, or even that the surfaces of the indium samples were considerably rougher than the gallium. It is even possible that a material such as indium, with an approximately isotropic Fermi surface and density of states,<sup>12</sup> could support diffuse scattering at the boundaries and still maintain pairing. It would be hard to imagine this to be possible with a highly anisotropic material such as gallium,<sup>13</sup> unless the pairs always recombined, after scattering, with that group of quasiparticles coming from the same  $\theta$  and  $\varphi$  directions originally. If this is done via specular reflection, the proper number of partners of equal and opposite momenta traveling along the same line of action (zero angular momentum) could be maintained.

The author wishes to thank Professor J. F. Cochran for the original suggestion of the search for a mfp effect in gallium single crystals. The computations were done at the Georgetown University Computation Center.

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\*This work was supported at Massachusetts Institute of Technology under Advanced Research Projects Agency Contract No. SD-90 and at Georgetown under Atomic Energy Commission Contract No. AT-(40-1)-3665.

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