

# On Different Types of Superconductivity

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Recent work on high field superconductivity has revived interest in the sponge model which I proposed, almost thirty years ago,<sup>1</sup> in order to explain the magnetic, electric, and calorimetric observations which we had made on alloys. Unfortunately, when recently quoting this old paper, some authors have arrived at a degree of misinterpretation which has given rise to quite unnecessary confusion of an issue which otherwise appears to be relatively simple.

Experimental evidence at present suggests that there exist two patterns of superconductive behavior which, in their "pure" form, appear to be quite distinct and well defined. Type I which is exemplified by pure mercury or tin single crystals was experimentally established by numerous careful investigations following immediately upon the discovery of the Meissner effect. In this type magnetic induction and electrical resistivity change suddenly and reversibly at a well-defined critical field, commonly denoted as  $H_c$ . This is the type usually described as the "ideal case" in standard textbooks, and for which Gorter's thermodynamical treatment<sup>2</sup> was developed.

The existence of pure type II superconductivity was experimentally established only in the last few years. However, the basic idea of this type which, instead of retaining zero induction, tends to split up into superconductive and normal regions was suggested in early theoretical papers by Gorter<sup>3</sup> and H. London.<sup>4</sup> These papers clearly envisaged two distinct types of superconductivity for which London accounted by different signs of the surface tension parameter, the reason for which was discovered by Pippard in 1953.<sup>5</sup> A somewhat similar treatment, based on the quantum mechanical ideas of Ginsburg and Landau, was given in 1957 by Abrikosov<sup>6</sup> who discussed the whole problem in some detail. All these theoretical considerations were based on the almost simultaneous discovery, in Oxford,<sup>7</sup> Leiden,<sup>8</sup> and

Kharkov,<sup>9</sup> that in alloys magnetic flux penetrates into the metal at a much lower field ( $H_{c1}$ ) than that ( $H_{c2}$ ), at which the resistance ceases to be zero.

None of these interpretations requires the application of the sponge model, although this was by no means certain at first. The sponge model was introduced in order to account, in terms of filaments of high threshold value, for the observed trapping of flux by assuming multiply connected arrays of such filaments. The decisive part played by lattice imperfections was immediately realized, but it was also pointed out that the filaments could occupy an appreciable fraction of the metal.

The question whether a separation of  $H_c$  into  $H_{c1}$  and  $H_{c2}$  requires the existence of lattice imperfections had to be left open, but the problem was fully realized at the time. The main reason for this was provided by our observation that not only alloys but also pure hard superconductors, such as tantalum, showed this behavior, and we then pointed out that: "Only further experiments on pure Ta specimens with undistorted lattice (if possible single crystals) can decide whether the splitting up in small supraconductive regions is spontaneous or caused by disturbances of the lattice."<sup>10</sup>

A year later we obtained much purer but still polycrystalline rods of Ta and Nb which trapped less flux,<sup>11</sup> and it was also noticed that the degree of trapping increased with falling temperature. However, it was encouraging that the specific heat discontinuity in the Ta rod agreed well with the steepness of the critical field curve.<sup>12</sup> At the same time in very pure samples of soft superconductors the changes of induction and resistivity were measured simultaneously,<sup>13</sup> and it was found that while in tin and mercury  $H_{c1}$  and  $H_{c2}$  coincided this was true for lead only at temperatures above  $\frac{1}{2}T_c$ . Below this,  $H_{c2}$  began to exceed  $H_{c1}$ . Since no flux was trapped, we could discount sponge structure, and suggested that

<sup>1</sup> K. Mendelsohn, Proc. Roy. Soc. (London) **A152**, 34 (1935).

<sup>2</sup> C. J. Gorter, Nature **132**, 931 (1933).

<sup>3</sup> C. J. Gorter, Physica **2**, 449 (1935).

<sup>4</sup> H. London, Proc. Roy. Soc. (London) **A152**, 650 (1935).

<sup>5</sup> A. B. Pippard, Proc. Roy. Soc. (London) **A216**, 547 (1953).

<sup>6</sup> A. A. Abrikosov, Zh. Eksperim. i Teor. Fiz. **32**, 1442 (1957) [English transl.: Soviet Phys.—JETP **5**, 1174 (1957)].

<sup>7</sup> T. C. Keeley, K. Mendelsohn, and J. R. Moore, Nature **134**, 773 (1934); K. Mendelsohn and J. R. Moore, Nature **135**, 826 (1935).

<sup>8</sup> W. J. de Haas and J. M. Casimir-Jonker, Nature **135**, 30 (1935).

<sup>9</sup> J. N. Rjabinin and L. V. Shubnikov, Physik Z. Sowjetunion **7**, 122 (1935).

<sup>10</sup> K. Mendelsohn and J. R. Moore, Phil. Mag. **21**, 532 (1936).

<sup>11</sup> J. G. Daunt and K. Mendelsohn, Proc. Roy. Soc. (London) **A160**, 127 (1937).

<sup>12</sup> K. Mendelsohn, Nature **148**, 316 (1941).

<sup>13</sup> J. G. Daunt, Phil. Mag. **28**, 24 (1939).

this was indeed a spontaneous splitting up into filaments under pure conditions. This conclusion was reached by supplementing our information with a determination of the thermal conductivity,<sup>14</sup> a method which we used widely in later years. Lead was investigated again with MacDonald in 1949,<sup>15</sup> and the same effect was found.

In 1956 I became aware of the existence of some Ta single crystals which had been made by Calverley, using an electron beam zone melting technique.<sup>16</sup> Measurements on this crystal revealed complete magnetic reversibility and practically ideal type I behavior.<sup>17</sup> An enormous phonon conductivity at about  $0.2T_c$  showed that it was free from strain. The same high phonon conduction was shown by a similarly prepared Nb crystal and this also showed high magnetic reversibility. In its magnetic behavior, however, it exhibited the type II pattern, the ratio  $H_{c1}/H_{c2}$  decreasing with falling temperature.

In view of the success which we had with specimens prepared in this manner, Calverley and Rose-Innes<sup>18</sup> set out to make single crystals of statistically disordered alloys of Ta with Nb, covering the whole concentration range. These, together with the Nb crystal mentioned above, were the first examples of pure type II behavior observed. They, too, show high phonon conductivity. Other investigations in recent years, particularly the beautiful experiments of Livingston<sup>19</sup> on lead alloys, have produced more information on this new type of superconductive behavior, but much remains unknown. Whereas  $H_{c1}$  is quite sharply defined, there is a fair amount of uncertainty about the position and significance of  $H_{c2}$ . The heat conductivity measurements, too, show some unexplained features. Two years ago, I reported<sup>20</sup> the observation that in high transverse mag-

netic fields the thermal conductivity of a Ta 70%-Nb 30% crystal falls far short of the value obtained by linear extrapolation of the normal state above  $T_c$ . We have now supplemented these results with data derived through the Wiedemann-Franz law from measurement of the electrical resistance on the same specimens. These data also differ from the heat conductivity results, but agree with the extrapolation from above  $T_c$ . The heat conduction suggests very low values of  $H_{c1}$ , and this is borne out by, admittedly rough, determinations of the magnetization. An interpretation of these observations will have to be deferred until more experimental information is available.

Nowhere in these considerations of pure type I or type II phenomena has it been necessary to invoke the sponge model. This indicates that the early assumption of sponge structure being the result only of lattice imperfections seems to be correct. Indeed, as I see the problem, pure type I and type II have been shown to exist, both being well defined and both showing magnetic reversibility. The sponge is *not* an alternative to type II, but a structure-dependent complication which may affect both types.

This does not mean, however, that the sponge is unimportant when high current-carrying capacity is considered. As was originally pointed out, the skeleton of the sponge carries high supercurrents, and this feature of the model has been elaborated by Bean.<sup>21</sup> An important advance in this question has been made in the last few months by Heaton and Rose-Innes,<sup>22</sup> who have measured the critical current in external fields of a Ta-Nb alloy wire when strained and again after annealing. They found that high current-carrying capacity vanished after annealing. In addition, they measured the magnetization curve in both cases and found that while the annealed wire gives the pure type II pattern, the strained one shows typical sponge behavior. We may therefore conclude that the feature permitting the construction of high field superconductive solenoids is not pure type II but the sponge.

<sup>14</sup> K. Mendelsohn and R. B. Pontius, *Phil. Mag.* **24**, 777 (1937).

<sup>15</sup> D. K. C. MacDonald and K. Mendelsohn, *Proc. Roy. Soc. (London)* **A200**, 66 (1949).

<sup>16</sup> A. Calverley, M. Davis, and R. F. Lever, *J. Sci. Instr.* **34**, 142 (1957).

<sup>17</sup> A. Calverley, K. Mendelsohn, and P. M. Rowell, *Cryogenics* **2**, 26 (1961).

<sup>18</sup> A. Calverley and A. C. Rose-Innes, *Proc. Roy. Soc. (London)* **A255**, 267 (1959).

<sup>19</sup> J. D. Livingston, *Phys. Rev.* **129**, 1943 (1963).

<sup>20</sup> K. Mendelsohn, *IBM J. Res. Develop.* **6**, 27 (1962).

<sup>21</sup> C. P. Bean, *Phys. Rev. Letters* **8**, 250 (1962).

<sup>22</sup> J. W. Heaton and A. C. Rose-Innes, *Appl. Phys. Letters* **2**, 196 (1963).