parallel domain structure during polarization reversal under the conditions given above, there are many important experiments which are possible and which will undoubtedly lead to a better understanding of ferroelectric $BaTiO_3$. Among those which the authors are currently investigating are the following: the phenomena which give rise the visibility of the antiparallel domains, the quantitative aspects of sidewise wall motion in metal-electroded crystals, the nucleation sites for reversed domains, the origin and characteristics of ferroelectric Barkhausen puises, and the effects of various electrodes and impurity dopings on the characteristics of polarization reversal.

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[1]For a general discussion of the published work on this subject, the reader is referred to W. Känzig, in Solid State Physics, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1957), Vol. 4.

[2]W. J. Merz, Phys. Rev. 88, 421 (1952). W. J. Merz, Phys. Rev. 95, 690 (1954).

[3]E. A. Little, Phys. Rev. 98, 978 (1955).

[4]D. Meyerhofer, Phys. Rev. 112, 413 (1958).

[5]J. A. Hooton and W. J. Merz, Phys. Rev. 98, 409 (1955).

[6]G. L. Pearson and W. L. Feldmann, J. Phys. Chem. Solids 9, 28 (1959).

[7]R. C. Miller, Phys. Rev. 111, 736 (1958).

[8]R. C. Miller and A. Savage, Phys. Rev. 112, 755 (1958).

[9]S. Triebwasser and E. F. Hahn, Bull. Am. Phys. Soc. Ser. II, 4, 184 (1959).

[10]R. C. Miller and A. Savage (unpublished).

SUPERCONDUCTIVITY OF β MERCURY*

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Solid mercury ordinarily crystallizes in a rhombohedral structure which is stable to absolute zero under normal pressures. Recent experiments have shown, however, that a new type of solid mercury can be produced which is actually the more stable form at temperatures below 79°K.[1] The first indications that this new modification existed were found in the course of a series of experiments in which the effect of pressure on the superconducting transition temperature of normal (α) mercury was studied.[2] The results of these experiments implied (although not conclusively) that the new (β) phase was also superconducting. The theory of superconductivity, as given by Bardeen, Cooper, and Schrieffer,[3] is relatively insensitive to the band structure, and, hence, for a given element, the superconducting transition temperature in zero field should be dependent to a first approximation only on the density.[4] Lanthanum, which is far from an ideal superconductor,[5] represents what has been the only known example of an element that exists in two superconducting crystallographic modifications. The two forms of mercury seemed to offer a more ideal opportunity for checking the dependence of the superconducting transition temperature on crystal structure, and in order to investigate this point we have recently investigated the initial part of the critical field curve for β mercury. The zero-field transition temperature which was found for β mercury can be explained quantitatively in terms of the known difference in molar volume[1] (about 1.5%) between the two forms of solid mercury, and the pressure-effect data for α mercury.[2]

Although β mercury is stable at zero pressure below 79°K, and metastable for temperatures below 90°K, it can be formed only at relatively high pressures (4000 atmos). Above 90°K the low-temperature β phase anneals rapidly into the α phase in an irreversible manner, so care must be taken in handling samples once they have been obtained. In our case, a fine wire of the β phase, 0.4-mm diam, was formed by extruding solid mercury under liquid nitrogen from a 0.250-in. diam cylinder through a 0.016-in. diam hold. A pressure of 8000 atmos was necessary to initiate extrusion, so β mercury was formed in the cylinder before the extrusion began. The extrusion rate was kept small (about one inch of wire per hour) in order to prevent local heating and annealing. A convenient, though destructive, test for the existence of the β phase was made by measuring the resistance of a piece of wire in liquid nitrogen before and after heating in air to 100°K. The existence of the β phase was indicated by an irreversible resistance increase of a factor of two due to the $\beta \rightarrow \alpha$ transition.

The critical field curve to 200 gauss was determined by placing the wire in the center of a small solenoid which was later placed in a liquid helium Dewar, all manipulations taking place under liquid nitrogen. The transitions were observed by using an ac mutual inductance method at 33 cps, with a measuring field of 0.02 gauss rms superimposed on the dc field. The results of three runs on both α and β mercury are given

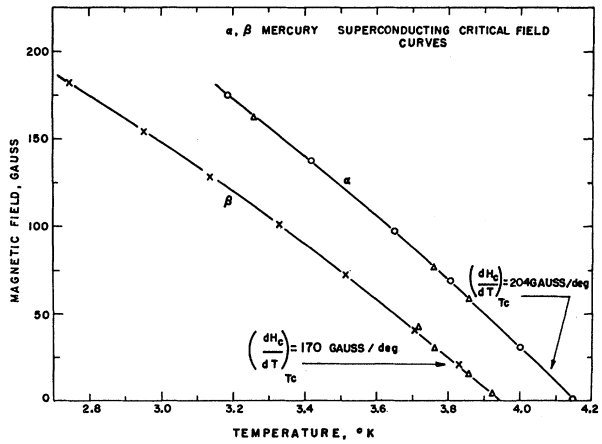

FIG. 1. The critical-field curves for the α and β forms of mercury.

in Fig. 1. In the first run, the sample (0.4-mm diam) was inadvertently allowed to warm above 90°K, and only the α transitions were noted. An identical piece of wire was used in the second run, and only the β transitions were found. Finally, a third run was made with a slightly larger wire (about 0.55-mm diam) which, for some unexplained reason, seemed to contain a mixture of both phases, and two sets of transitions were found, neither being of the same quality as in the first two runs. The consistency within a given run was about ± 0.1 gauss, with an agreement between different runs of about one gauss. The wire used in the first two runs may have been fairly strain-free, since it had been kept under liquid nitrogen for two weeks before the runs were made. The second lot of wire was run almost immediately after extrusion, and may have been quite strained, since changes in hardness of the wire with time have been observed in the course of this work. Thus, we tend to rely on the first two runs as being the more dependable, and on the third run as furnishing a qualitative confirmation of the first two.

The changes in both the zero-field transition temperature (from 4.1536°K for α mercury to 3.94°K for β mercury) and the shape of the critical-field curve are quite marked. Our data for α mercury agree with Maxwell and Lutes[6] in that, within our accuracy and the limited range of our magnetic fields, the critical-field curve is strictly parabolic, with an H_0 of 426 gauss, compared with their 410 gauss. The critical-field curve for β mercury appears to deviate appreciably from parabolic shape in the same sense as tin and indium, although no attempt was made to fit the data to an analytic curve to determine a value for H_0. The measured initial slopes of the critical-field curves are -204 gauss/deg for α mercury and -170 gauss/deg for β mercury.

The change in the zero-field transition temperature (-0.21°) can be explained almost completely by the change in volume due to the crystallographic transformation. The pressure-effect experiments[2] give $(dT_c/dV) = 0.91$ deg/(cm^3/mole), and the compression measurements give $\Delta V = V_\alpha - V_\beta = 0.206$ cm^3/mole at 4°K.[1] Thus, on the basis of these data, a change in T_c of -0.19° would be predicted, well within the experimental uncertainties. On the basis of this same assumption, the observed difference in the slopes of the critical-field curves can be explained only if $(\partial H_c/\partial V)_T$ were to increase with decreasing temperature. This does not correspond with what is known of any other superconductor,[7] and we hope to investigate this point at a later date.

An x-ray powder camera for use at either liquid nitrogen or liquid helium temperatures was constructed in order to determine the structure of β mercury. The results of this work are only tentative, but the pictures which have been obtained show conclusively that the structure of β mercury is quite different from that of α mercury. The powder diffraction patterns from β mercury can be explained by a body-centered tetragonal structure, although a definite statement cannot be made until further data are obtained.

The authors are indebted to Dr. M. Atoji for his collaboration in the design of the x-ray cryostat, and for his determination of the structure from the pictures which were taken. More complete accounts of the x-ray and superconductivity experiments will be published as separate papers at a later date.

*Contribution No. 728. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

[1]C. A. Swenson, Phys. Rev. 111, 82 (1958).

[2]L. D. Jennings and C. A. Swenson, Phys. Rev. 112, 31 (1958).

[3]Bardeen, Cooper, and Schrieffer, Phys. Rev. 108, 1175 (1957).

[4]For a discussion of the effects of crystal structure, see D. Pines, Phys. Rev. 109, 280 (1958).

[5]Anderson, Legvold, and Spedding, Phys. Rev. 109, 243 (1958).

[6]E. Maxwell and O. S. Lutes, Phys. Rev. 95, 333 (1954).

[7]J. L. Olsen and H. Rohrer, Helv. Phys. Acta 30, 49 (1957).