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CORRESPONDENCE

Evidence for a Third Phase of Mercury

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Abstract

It has been found that tensile deformation at liquid helium temperature partially transforms α-mercury to a γ phase which is distinguished from the α and β phases by having a lower superconducting critical field curve and a lower transition temperature ($T_{c\gamma}=3{\cdot}74\pm0{\cdot}05$°K compared with the values found by Schirber and Swenson (1961), $T_{c\alpha}=4{\cdot}153$°K and $T_{c\beta}=3{\cdot}949$°K). Resistance measurements show that the γ phase transforms back to α-mercury at about 53°K.

The simple rhombohedral α phase of mercury remains unchanged at atmospheric pressure down to liquid helium temperatures (Barrett 1957). Bridgman (1935) first observed a transition under pressure to the β phase, which was found to have a body-centred tetragonal structure by Atoji, Schirber and Swenson (1959). Swenson (1958) found that this β phase, once formed, was stable at atmospheric pressure up to 79°K, at which temperature it transformed back to the α phase. High pressure was found to be necessary and in addition shear was helpful in forming the β phase, and Schirber and Swenson (1962) suggested that the transformation was martensitic in nature. In the present investigation we have found that simple tensile deformation of α-Hg at 4·2°K partially transforms it to a phase which has a lower superconducting transition temperature and critical field curve than those of either the α or β phases as found by Schirber and Swenson (1961); we therefore call it the γ phase.

For superconducting magnetization measurements rod specimens 7 cm long and 2·4 mm diameter were prepared from triply distilled mercury having about 1 p.p.m. non-gaseous impurities. The rods were gripped in a simple tensometer and pulled in tension in liquid helium. The magnetization M was determined from fluxmeter deflections on moving a pair of oppositely wound co-axial coils from one position around the middle of the specimen to another remote from the specimen; in both positions there was zero mutual inductance between the empty coil pair and the field coil.

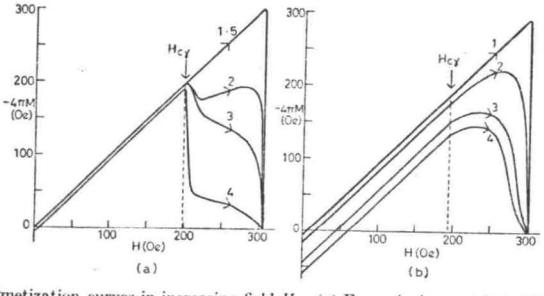
Evidence for the γ phase is shown in the magnetization curves of figs. 1 (*a*) and (*b*), which were obtained in increasing field from, respectively, a

single crystal and a polycrystal of mean grain size 2 mm. Prior to recording each magnetization curve the magnetic field had been increased to a value greater than the critical field $H_{c\alpha}$ for the α phase and then had been reduced slowly to zero, leaving the specimens with some trapped flux. After obtaining the curves 1 to 4 of fig. 1 (*a*), which show the progressive effect of increasing deformation, the single crystal specimen was annealed for 12 hours at a temperature near 77°K after which the magnetization curve 5 taken at 2·11°K reverted to that for the pure α phase. Three other nearly single crystals were strained at liquid helium temperatures, two of which yielded magnetization curves similar to those of fig. 1 (*a*) but with less pronounced inflexion; the third yielded curves similar to those of fig. 1 (*b*) for a polycrystalline specimen. All sets of curves have the following features in common:

(i) The field at which $-4\pi M$ falls to zero remains approximately unchanged throughout the deformation and is the critical field $H_{c\alpha}$ of the α phase.

(ii) The field at which the magnetization first deviates from the perfect diamagnetic also remains unchanged throughout the deformation; this we identify as the critical field $H_{c\gamma}$ of the supposed γ phase.

Fig. 1

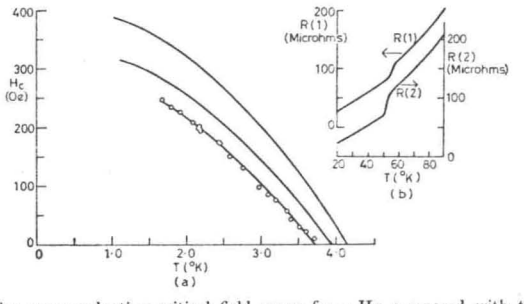


Magnetization curves in increasing field H. (*a*) For a single crystal at 2·11°K: curve 1, unstrained; 2, 2·8%; 3, 5·7%; 4, 13·3% strained at 2·11°K; curve 5, after anneal near 77°K; (*b*) for a polycrystal at 2·16°K: curve 1, unstrained; 2, 5·5%; 3, 11·1%; 4, 22·2% strained at 2·16°K.

The variety of shapes of the magnetization curves between the extremes of figs. 1 (*a*) and (*b*) is probably due to differences in orientation of the transformed regions relative to the specimen axis; there is some evidence from surface traces left on the rods that these regions are platelets, spanning the whole cross section in some of the monocrystalline specimens. In the

hypothetical case of a specimen split up into plates of α and γ phase parallel to the rod axis one would expect a linear superposition of two type I magnetizations, and curve 4 of fig. 1 (*a*) is the nearest approach to this case. For all other orientations of the plates the magnetization behaviour in the range of fields $H_{c\gamma}$ to $H_{c\alpha}$ will be complicated by the formation of the superconducting intermediate state and by the screening of γ regions by α regions.

Fig. 2



(*a*) The superconducting critical field curve for γ-Hg compared with those for α and β-Hg as determined by Schirber and Swenson (1961); (*b*) the resistances R(1) and R(2) of two specimens, previously strained about 30% at 4·2°K, as a function of increasing temperature showing the transformation back to α-Hg at about 53°K.

The critical field curve for the γ phase is shown in fig. 2 (*a*) together with those for α and β-Hg found by Schirber and Swenson (1961). Values of $H_{c\gamma}$ were found from feature (ii) above, as shown in fig. 1, from results on three specimens which had been strained about 30% at 4·2°K, and on three others which had been strained at a temperature below $T_{c\gamma}$. Extrapolation yields a value $T_{c\gamma} = 3{\cdot}74 \pm 0{\cdot}05$°K, compared with $T_{c\beta} = 3{\cdot}949$°K and $T_{c\alpha} = 4{\cdot}153$°K (Schirber and Swenson 1961).

The increase of resistance on warming up two typical specimens which had previously been strained about 30% at 4·2°K is shown in fig. 2 (*b*); the temperature, 53 ± 3°K, of the sharp increase is reproducible, and no further steps were observed up to 100°K. From this, and from curve 5 of fig. 1 (*a*), it can be concluded that the γ phase transforms directly back to the α phase. The magnitude of the step at about 53°K varies from one specimen to another, presumably according to the degree of transformation achieved. The magnetization measurements, such as are shown in fig. 1 (*a*) for a specimen of favourable crystallographic orientation, suggest that the fraction by volume of transformed material increases rapidly with strain up to about 5%

and then subsequently less rapidly. Optical examination of surface traces on the same specimen indicated that about half was transformed by a strain of 13%.

A study of the crystallography of the transformation, including an x-ray diffraction determination of the structure of the γ phase, has been initiated in this Department. It is of interest that Weaire (1968) has predicted on the basis of pseudopotential theory that the γ structure might be obtained from face-centred cubic by the opposite rhombohedral distortion to that which produces the α structure (regarded as face-centred rhombohedral). Another possibility considered by Weaire (1968) is a distorted hexagonal close-packed structure with c/a about 2·0.

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Step Growth on Ice during the Freezing of Pure Water

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Abstract

Ice has been observed to grow from its pure melt by the propagation of steps across the freezing interface. The heights of the steps range from 0·1 to 4 microns and the distance between steps from 5 to 20 microns. The concentration of steps and their behaviour appear to be completely independent of crystal orientation.

Several workers have obtained indirect experimental evidence which indicates that when ice grows in the direction of the c axis into supercooled water it does so by the propagation of steps across the basal plane (Hillig 1958 Michaels, Brian and Sperry 1966). Hillig and Turnbull (1956) found that the growth of ice normal to the c axis was proportional to the 1·7 power of the supercooling of the water. They concluded from this result that growth in this direction also was probably controlled by step growth. In this note we described the results of experiments in which steps have been observed to move across the freezing interface of polycrystalline ice growing slowly from pure water.

The experimental apparatus consisted of a stainless-steel box with glass cover-plate (fig. 1). The box was cooled by means of a thermoelectric module attached to the bottom of the box. The entire assembly was mounted on the micrometer stage of a microscope so that the ice–water interface could be conveniently viewed. Prior to freezing, a vacuum system was used to remove all air from the box. The water was singly distilled and was passed through an ion exchange column. After the water had been slightly supercooled it was nucleated either by giving the box a sharp rap or by passing a rod cooled in liquid nitrogen over the surface of the water. A short time after the freezing was initiated the ice–water interface became parallel to the bottom of the box and the polycrystalline ice consisted of grains about 0·3 mm^2 in area. The freezing rates were in the range of 0·1 to 1 micron sec^{-1}.

When the water above the ice was essentially isothermal, steps were observed to move over the entire freezing interface (fig. 2). Some of these steps originated at grain boundaries while others grew from spiral