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Pressure Dependence of Superconducting Transition Temperature of High-Pressure Metallic Te

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Existing data at high pressures of Berman, Binzarov, and Kurkin show that the various metallic forms of Te have considerable variation of their superconduction temperatures, T_c, depending upon the phase and the pressure; the observed T_c's ranged from 2.5 to 4.3°K over the pressure span of 40 to 150 kbar. The present experiments, with use of a diamond-tipped apparatus with a cryogenic arrangement, have extended the pressure range to over 300 kbar. The results indicate that a new metallic phase develops in the 150–180-kbar region, which has a higher T_c of about 6.5°K.

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Many covalently bonded crystalline materials such as Si, Ge, Te, Se, etc., which are insulators or semiconductors in their usual low-pressure forms, transform to metallic phases under sufficient pressure,[1-4] some of these "high-pressure metals" exhibit superconductivity at low temperatures.[5-9] In 1973, Berman, Binzarov, and Kurkin[9] (BBK) published their results for an extensive series of high-pressure cryogenic experiments with Te in which they explored the T_c of the metallic forms of Te over the pressure range of about 38–260 kbar (which corresponds to about 38–150 kbar on the modern pressure scale.[10, 11]) Their findings are shown here in Fig. 1, in which T_c is plotted against P (modern scale). They concluded that in this range there are three different metallic phases: the first (38–60 kbar) having an unusually large positive dT_c/dP; the second (60–75 kbar) with a nearly zero dT_c/dP; and the third (75 kbar and up) with a strong negative dT_c/dP.

With our new apparatus[12] one of the early runs (to test the apparatus and procedure) was made with a specimen of Te because it was known to be superconducting. The run was made at about 220 kbar. This specimen exhibited an excellent superconduction transition as shown in Fig. 2, but at a much higher temperature than observed by BBK. This discrepancy indicated that Te may have a different metallic phase at the higher pressure.

This report gives the results of a recent series of experiments done with our apparatus[13] in which a specimen was compressed at room temperature in eight successive steps from 50 to 305 kbar and was tested at each step for superconductivity by cooling it to about 2.7 °K. At the lower pressures our results agree moderately well with those of BBK, and at higher pressures a new metallic phase with the higher T_c does indeed develop, as was suggested by our earlier experiment.

The series of tests spanned a period of 44 days, as each warmup took a few days of time. After warming through the T_c zone, measurements were taken of the resistance of the "normal-state" metal on up to room temperature to provide information for determining the Grüneisen "characteristic temperature" of electrical conductivity, Θ.[14]

The room-temperature resistance behavior during the eight stepwise loadings is shown in Fig. 3(a). The room-temperature electrode resistance of about 0.18 Ω needs to be subtracted from the values shown in order to get the specimen resistance. Note that during the first cryogenic temperature cycle, at 7.2 tons loading, the room-

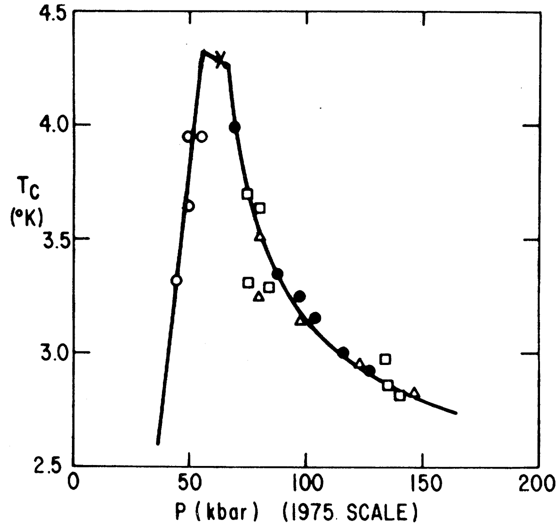

FIG. 1. The 1973 data of BBK on $T_c(P)$ of Te (pressure scale revised to modern scale) (see Refs. 10 and 11).

temperature resistance of the specimen decreased from 2.6 to 0.95 Ω. In the later T cycles at higher loadings, the resistance change during the cycling was much less. Probably the first cycle promoted fairly complete conversion of the specimen to a metallic form.

Figure 3(b) shows the superconduction transitions of the specimen at various pressures. It is seen that below 100 kbar the transitions are quite sharp, and that the one for 70 kbar is definitely at a slightly higher temperature than the ones at 50 and at 95 kbar. This is roughly in agreement with the data of BBK. Between 125 and 165 kbar it is seen that the step in the $R(T)$ curve in the superconduction transition region starts to shift in the higher-temperature direction, and also changes shape by tapering off at the high-temperature end. By 195 kbar the top knee of the $R(T)$ curve has reached the 6.8 °K value which we observed in our first test experiment at 220 kbar, but there still remains some of the earlier phase with the lower T_c. By 305 kbar in this present series the specimen appears to have nearly completely transformed to the higher-pressure phase having the higher T_c.

Between about 150 and 280 kbar the curves in Fig. 3(b) indicate that there is a mixture of two phases in the specimen, each having its superconduction transition drawn out over a considerable temperature interval. One way of analyzing this is to mark the limits of the segments and plot these on a $T_c(P)$ chart, as in Fig. 4. According to this method of analysis it is seen that in the 150–250-kbar phase-overlap region the mid-T_c of each phase increases with pressure, and finally at about 280 kbar, the mid-T_c of the higher-pressure phase levels out at about 6.3 °K.

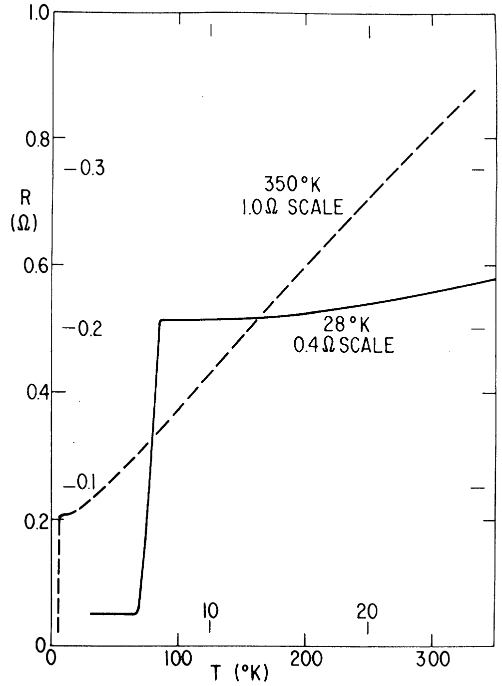

FIG. 2. Our earlier data on $R(T)$ of Te at about 220 kbar. Note the large superconduction step between 5.5 and 6.8 °K.

In the same chart the results of BBK are shown for comparison with ours. The agreement is fairly good for the mid-range values and the variations with pressure but the data of BBK show considerably greater amplitude of variation of T_c with pressure. We do not believe that this can be explained on the basis of pressure gradient in our specimen because the cell geometry of our apparatus provides for less pressure gradient than that of BBK's cell. This is demonstrated by the sharpness of our 50-kbar $R(T)$ transition relative to that of BBK (Ref. 9).

Another comparison of interest is between our 240-kbar curve of Fig. 3(b) and our 220-kbar curve in Fig. 2. In the former the lower part of the curve indicates a considerable residue of the lower-pressure phase whereas in the latter the transition appears to be almost entirely of the higher-pressure phase. The operational difference was that in the 220-kbar case the specimen was compressed directly to the test pressure, while in the 240-kbar case the compression had

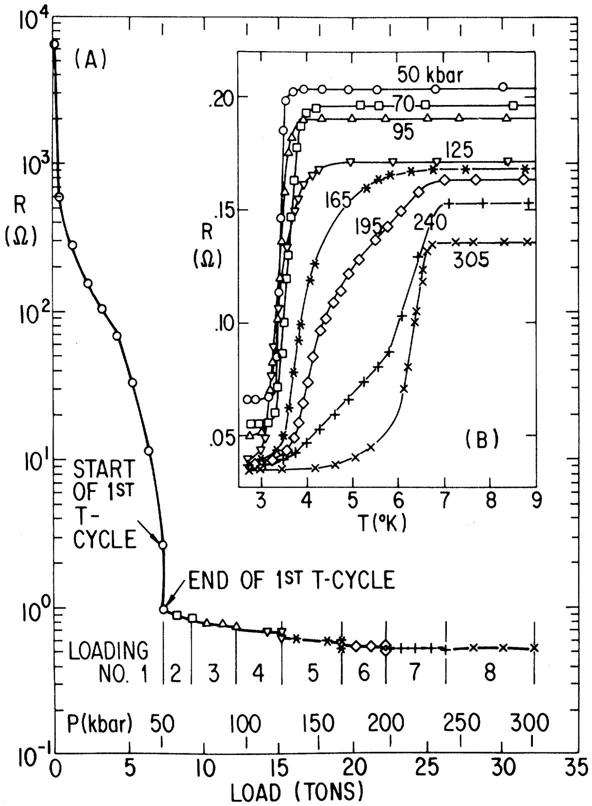

FIG. 3. (a) R vs L (or P) during the stepwise room-temperature loadings of the specimen. (b) $R(T)$ at various pressures in the superconducting transition temperature region.

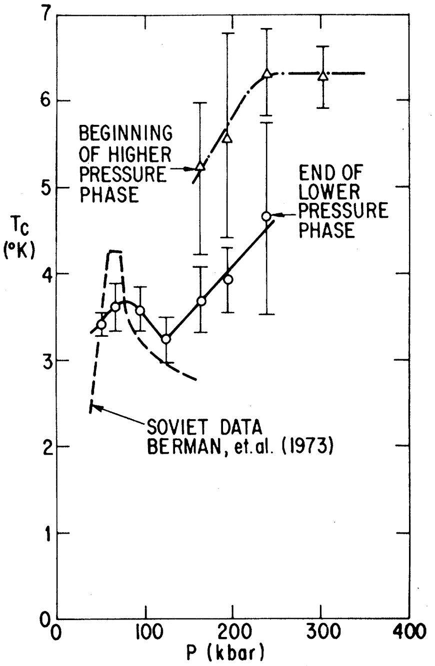

FIG. 4. T_c vs P for Te superconduction transitions.

been in seven successive steps with cryogenic cycles made at each step. Perhaps in the long drawnout stepwise procedure with temperature cycling the crystallites of the lower-pressure phase became larger and more stabilized and resisted transformation to the higher-pressure phase. Similar behavior was observed for Se specimens[4] where it became evident that there was competition by a mid-pressure semiconducting phase which could be nearly bypassed by a direct, single compression.

The resistance behavior $R(T)$ of the metallic forms at temperatures above T_c are of interest from the point of view of their residual resistance and of their "characteristic temperature." The method which we used for analyzing the data consisted of the following steps: First, the $R(T)$ of the electrodes was subtracted from the total measured $R(T)$ to give the specimen $R(T)$ which consists of the residual resistance (which is independent of T) plus the "true metal resistance." The latter, according to theory, varies as T^5 at very low temperatures, and then becomes linear with temperature as the temperature increases. Extrapolation of the linear part to lower temperatures yields an intercept with the residual-resis-

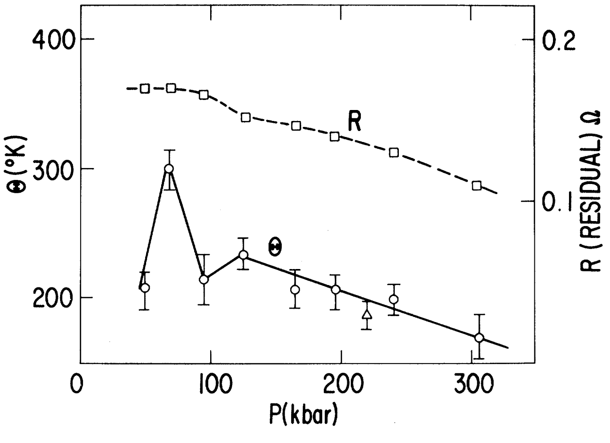

FIG. 5. Characteristic temperature Θ vs pressure for high-pressure Te metallic forms, and residual resistance vs pressure of the "normal" metallic Te in the pressure-step series. On the Θ curve, the one triangle datum point corresponds to the original 220-kbar, single-compression experiment. Accurate quantitative comparison of the "residual resistance" in the 220-kbar experiment cannot be made because there may have been slightly different length and width of the specimen relative to that of the stepped-pressure experiment.

tance line, and by theory the characteristic temperature (similar to the Debye temperature Θ_D for specific heats but not the same) is this intercept temperature divided by 0.1453.[14-17]

The experimental $R(T)$ curves from T_c up to room temperature for the eight different pressure runs had the same general appearance as the one shown in Fig. 2 for the original 220-kbar experiment. Each of these curves was analyzed in the manner described above to yield values of the characteristic temperature Θ. The results are presented in Fig. 5. The graphical analysis for Θ is admittedly approximate and the data points in Fig. 5 are given realistic error bars. The relatively high value of about 300 °K at 70 kbar appears to be real and seems to be associated with the high value of T_c at that pressure found by BBK,[9] and by us (Fig. 4). In the pressure range of 125–305 kbar, where the lattice stiffness of the metal would be expected to increase and produce a higher Θ, the experimental data show a decrease of Θ with pressure. This is a matter for further investigation, both experimental and theoretical.

The residual resistance versus pressure, shown in Fig. 5, indicates that this resistance decreases slowly with pressure. A quantitative analysis of this curve is not justified because the geometry of the specimen and of the electrodes probably changed slightly due to the increase in loading. However, these variances are small enough in comparison to the residual resistance that the down slope can be considered to be real. This would suggest that the increase in pressure tends to heal, or eliminate, some of the electron scattering centers that are responsible for the residual resistance.

In this work we have studied the electrical resistance behavior of Te over a pressure range twice as great as formerly reported and find that Te continues to act as a normal metal at the higher pressures, but that in the 200-kbar region the T_c of superconductivity changes rather abruptly from the 3 °K region to well over 6 °K. These new observations resolve the discrepancy between our original observation of a T_c of about 6.5 °K at 220 kbar and the value of less than 3 °K indicated by the 1973 work of BBK. It is possible that this drastic change is a result of a phase change in the metal. It is suggested that this be studied by x-ray diffraction and other methods in apparatus capable of sustaining this very high pressure.

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