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Observation of anomalies in the pressure dependence of the superconducting transition temperature of potassium-based graphite intercalation compounds

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(Received 6 July 1982)

Measurements of the pressure (P) dependence of the superconducting transition temperature T_c of KC_8 and $KHgC_4$ are reported. KC_8 undergoes a first-order transition from a $T_c = 0.13$ K to a $T_c = 1.7$ K phase over the range $2 \leq P \leq 15$ kbar. A $KHgC_4$ sample underwent an anomalously broad superconducting transition at ambient pressure with an onset near 1.4 K, which is nearly double previously reported T_c values. The $KHgC_4$ transition sharpened dramatically for $P \gtrsim 1$ kbar and exhibited a strongly negative dT_c/dP at higher pressures. KC_{24} was found to be nonsuperconducting to $P = 10$ kbar and $T \geq 0.07$ K.

The layered structure of graphite intercalation compounds (GIC) and their unique "staging" behavior,[1-3] whereby each intercalant layer is regularly spaced between groups of n carbon layers ($n \equiv$ stage number), suggest that it might be possible to observe "quasi-two-dimensional" superconductivity in higher stage GIC's.[4-7] Although Hannay *et al.*[4] discovered superconductivity in stage-one alkali GIC's sometime ago, no superconductivity has been observed in these materials for $n > 1$, and conflicting values of $T_c \lesssim 0.5$ K have been reported for stage-one K, Rb, and Cs compounds studied in several different laboratories.[7-10] It is of interest to relate these facts to recent observations[11,12] of high-pressure phase transitions in KC_{24} and KC_8.

The Hg-amalgam GIC's have also proven to be particularly important since superconductivity was recently observed in *stage-two* $KHgC_8$ (Ref. 13) and $RbHgC_8$ (Refs. 14 and 15) at surprisingly high T_c's = 1.9 and 1.5 K, respectively. The subsequent observation[7] of relatively low T_c's for the corresponding *stage-one* $KHgC_4$ ($0.7 \lesssim T_c \lesssim 0.9$ K) and $RbHgC_4$ ($T_c = 1.0$ K) compounds poses some perplexing questions concerning crystal anisotropy and other factors which could govern T_c in these materials.[4-7] For example, stage-one $KHgC_4$ has been suggested to have a higher electronic density of states than stage-two $KHgC_8$, whereas the latter compound has both a higher T_c and greater anisotropy of the upper critical magnetic field.[7,13-15]

We report the results of high-pressure T_c measurements on stage-one KC_8 and $KHgC_4$ and on stage-two KC_{24}. Our data reveal strong anomalies in both the ambient and high-pressure superconducting behaviors of the stage-one compounds which contrast with T_c vs P data previously obtained[6] for stage-two $KHgC_8$. The stress- and sample-dependent effects documented in the present study offer new insight into the phase stability of GIC's and the irreproducibility of their superconducting properties. We would suggest that details of the elastic properties and/or subtle changes in crystallographic order may be very important in determining the T_c's of GIC's, and that the "intrinsic" values of T_c for particular phases of these materials are still uncertain.

Very low-temperature–high-pressure experiments were carried out at $P \lesssim 10$ kbar and $T \gtrsim 70$ mK using small miniature piston-in-cylinder clamp devices.[16] Details concerning sample preparation and additional apparatus used to generate hydrostatic pressures $P \lesssim 20$ kbar at $T \gtrsim 1.3$ K are described elsewhere.[6] All samples were analyzed prior to pressurization via x-ray diffraction and found to be of single stage with appropriate c-axis repeat distances.

Inductive data for KC_8 "sample 1" are shown for several values of applied pressure in Fig. 1. A very sharp room-pressure superconducting transition of width $W = 6$ mK was observed at $T_c = 0.130$ K,[17] in

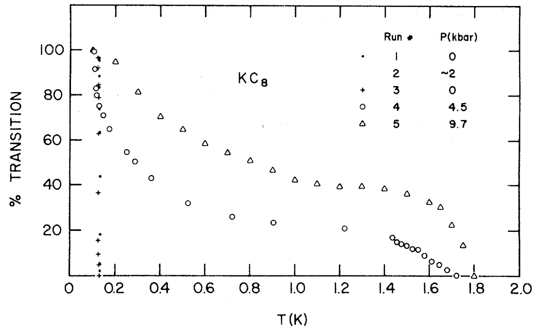

FIG. 1. Percent completion of the inductively measured superconducting transition of KC_8 sample 1 vs temperature T at various pressures P. The experimental runs are numbered in temporal sequence. The Sn manometer transition could not be detected in run 2, and those results are not plotted.

very good agreement with the most recent results of other investigators.[7,8] The application of a small pressure ≈ 2 kbar resulted in a severe broadening of the transition (not shown on Fig. 1) which stretched from an onset at 1.73 K to a termination at 0.11 K. The T_c of a Sn manometer could not be detected during this run (run 2), so another Sn manometer was substituted. The KC_8 sample was then remeasured at room pressure and a single, narrow transition ($W = 6$ mK) was again observed at $T_c = 0.127$ K. At 4.5 kbar, the transition signal again broadened considerably with an onset near 1.71 K and a termination at 0.105 K. A further pressurization to $P = 9.7$ kbar resulted in what appeared to be a "two-step" transition consisting of an "upper T_c" $\approx 1.7 \pm 0.1$ K and a broad "lower T_c" $\approx 0.5 \pm 0.4$ K. Such a step anomaly indicates the presence of appreciable amounts of at least two competing phases.

Experiments on a second KC_8 sample, 2, were carried out in ^4He with a larger pressure clamp,[6] and the results are shown in Fig. 2. Searches for superconductivity were conducted at room pressure, 3.4, 7.9, and 11.2 kbar, and no transition was detected to a limiting temperature $\simeq 1.30$ K. Further increments in pressure to 15.5 and 19.6 kbar resulted in observation of single, narrow transitions with $W = 50-80$ mK and $T_c \approx 1.8$ K. We saw no evidence for a second, lower transition at these temperatures and pressures. The subsequent withdrawal of pressure to 1.5 kbar failed to return T_c to values below 1.3 K. The final release of pressure to 1 atm resulted in the absence of a transition signal at $T \gtrsim 1.30$ K.

Fuerst *et al.*[12] have observed a discontinuous increase in the room-temperature *c*-axis electrical resistivity of KC_8 at $P \approx 15$ kbar. This result is consistent with the sudden appearance of superconductivity at $T_c \approx 1.7$ K in sample 2 at $P = 15.5$ kbar. The observation of considerable pressure-induced hystersis, and appreciable transition broadening on the depressurizing cycle (Fig. 1), imply the existence of a first-

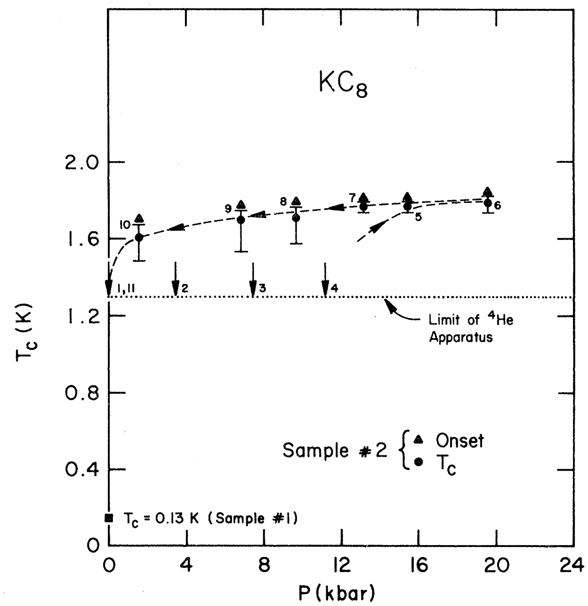

FIG. 2. Superconducting transition temperature T_c vs pressure P for KC_8 (sample 2). The data points are numbered in increasing temporal order. The 1-bar data point (□) for sample 1 is also indicated.

order phase transition at a pressure $11 \lesssim P_c \lesssim 15.5$ kbar. A plot of $\Delta T_c \equiv T_c(P) - T_c(0)$ vs P for sample 2 reveals a change in slope at a pressure $P_c \approx 13 \pm 1$ kbar, which is the basis for our estimate of the *low-temperature* transition pressure.

The data shown in Figs. 1 and 2 suggest that small amounts of stress can generate and metastably retain the high-pressure phase of KC_8. We note that effects due to various pressure media, sample defects, and nonhydrostatic stresses have been discussed by several investigators.[3,11,12]

Solin has suggested[18] that the room-temperature transition in KC_8 at 15 kbar may be due to a change in *c*-axis stacking sequence. If this supposition were true, our present results imply that a rather subtle change in crystal structure results in an *order of magnitude* change T_c (i.e., 0.13–1.7 K).

Successive dilution refrigerator measurements of stage-two KC_{24} carried out at pressures $P = 1$ bar, 2.7, 6.0, 7.5, and 10.1 kbar failed to detect superconductivity to a limiting temperature of 70 mK. This result has important implications for the minimum "dimensionality" requisite for superconductivity to occur in GIC's.[4,5] Clarke *et al.*[11] have concluded from high-pressure x-ray diffraction measurements that stage-two KC_{24} undergoes a transformation into a mixed stage-two–stage-three region for $P \gtrsim 2$ kbar, and that a pure stage-three phase is achieved in highly oriented pyrolytic graphite-based samples for $P \gtrsim 6$ kbar. Fuerst *et al.*[12] have observed a discontinuous decrease in the *c*-axis electrical resistivity of KC_{24} at $P \approx 3.5$ kbar, followed by an additional step increase of the resistivity at $P \approx 7.5$ kbar. Both of these results confirm the existence of at least one first-order phase transition at pressures well within our present experimental range.

The x-ray data[11] are consistent with the presence of a stage-one (KC_8) intercalant layer density in the high-pressure stage-three phase of KC_{24}.[18] If the interactions between a relatively dense intercalant layer and the two adjacent C bounding layers dominate the occurrence of superconductivity in GIC's, the high-pressure stage-three phase of KC_{24} would be a candidate for a quasi-two-dimensional superconductor consisting of widely spaced, dense K layers. With the reasonable assumption that we successfully induced a substantial amount of the stage-three phase of KC_{24} in the present experiments, we have found important evidence to suggest that superconductivity cannot exist in the quasi-independent intercalant layers for stage $n > 2$ GIC's.

The results of several dilution refrigerator experiments on a stage-one $KHgC_4$ sample at various pressures are shown in Fig. 3. The inductive signal from an initial room-pressure run indicated a very broad superconducting transition with an onset near 1.42 K and a termination near 0.85 K. The termination temperature is close to the T_c's $= 0.7 - 0.9$ K previously reported[7] for $KHgC_4$. However, our room-pressure onset temperature of 1.42 K is a new and unexpected result. The application of a modest pressure $P = 0.8$ kbar resulted in a remarkable sharpening of the transition and an increase of T_c to 1.49 K with $W = 37$ mK. Further increases in pressure resulted in sharp transitions at successively lower temperatures as shown in Fig. 3. Above $P = 0.08$ kbar, $dT_c/dP \approx -4.9 \times 10^{-5}$ K/bar, comparable to $dT_c/dP = -6.5 \times 10^{-5}$ K/bar previously observed[6] for stage-two $KHgC_8$. The subsequent release of applied pressure resulted in a transition signal which was again broad with an onset near 1.42 K, but the transition region had narrowed from a previous value of ~ 0.6 to 0.4 K.

The first measurement of T_c vs P for a GIC was recently performed on stage-two $KHgC_8$.[6] T_c was found to monotonically decrease in an anomaly-free fashion, similar to the behavior of most three-dimensional, *sp*-metal superconductors such as Sn. In contrast, the broad room-pressure transitions of $KHgC_4$ shown in Fig. 3 and the sudden pressure-induced enhancement of T_c, followed by a narrowing of the transition and a decrease of T_c with further applied pressure, are similar to effects observed in other anisotropic, charge-density-wave (CDW) materials

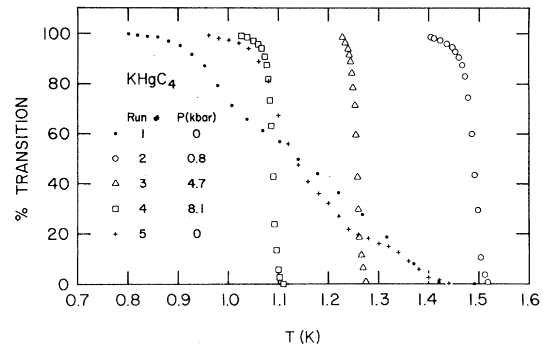

FIG. 3. Percent completion of the inductively measured superconducting transition of $KHgC_4$ vs temperature T at various pressures P. The experimental runs are numbered in temporal sequence.

such as $NbSe_3$.[6,19] It is possible that only a very small amount of pressure is necessary to destabilize a hypothetical CDW which could be present in $KHgC_4$ only near $P \approx 1$ bar. The presence of such a CDW would explain the broadened and suppressed T_c at room pressure and the negative dT_c/dP and narrower T_c's observed (after the CDW is suppressed) at high pressures.[6,20] Further work is necessary to directly test this interesting possibility. Similar considerations may also apply to high-pressure T_c data for KC_8.[21]

We have demonstrated that high-pressure superconductivity measurements can be a useful and convenient tool for studies of the phase stability, staging, degree of sample perfection, and the "dimensionality" of GIC's. Our results have important implications for resolving discrepancies between the ambient pressure experimental results of several laboratories, and lend convincing support to previous observations[11,12] of high-pressure phase transitions in KC_8. A more extensive analysis of our data in terms of recent theories[3,22–24] of the electronic structure, superconductivity, and staging behavior of GIC's will be presented in a future publication.

ACKNOWLEDGMENTS

Research at the University of Kentucky was support by the U.S. Department of Energy under Contract No. DE-AS05-81ER10936. Research at the University of California, San Diego was supported by the U.S. Department of Energy under Contract No. DE-AT03-76ER70227.

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