

## Enhanced superconductivity in hydrogenated potassium-mercury-graphite intercalation compounds

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Stage-1 potassium-mercury-graphite intercalation compounds with markedly different superconducting transition temperatures  $T_c$  and transition widths  $\Delta T_c$  are found to have uniformly high  $T_c$  and narrow transitions after exposure to hydrogen. These hydrogen-doping experiments suggest a schematic model for the density of states in stage-1 potassium-mercury-graphite intercalation compounds.

One particularly active area of research in recent years has been the study of the effects of hydrogen absorption on metals.<sup>1</sup> Among the many results of hydrogen uptake are changes in superconductivity. For example, in some transition metals, hydrogen absorption causes an increase in the superconducting transition temperature  $T_c$ , while in others  $T_c$  decreases upon hydrogenation.<sup>2</sup> The introduction of hydrogen has previously been shown to increase the transition temperature of one graphite intercalation compound:  $C_8K$ .<sup>3</sup> The transition temperature depends strongly on the details of the band structure near the Fermi level. Therefore, one cannot generalize from a single example about the effect of hydrogenation on other graphite intercalation compounds, just as it was difficult to generalize about the transition metals.

The stage-1 potassium-mercury-graphite intercalation compounds (KHg-GIC's) are especially interesting from the standpoint of superconductivity. Discussions of the nature of the superconductivity in these compounds have been greatly complicated by widely varying values reported for the superconducting transition temperature  $T_c$ , which has ranged from the 0.8 K initially found<sup>4</sup> up to 1.5 K both with<sup>5</sup> and without<sup>6</sup> the application of external pressure. Structural and stoichiometric distinctions among samples have been cited as the source of variation among them. Previous attempts to understand the differences among samples focused on their intercalation conditions.<sup>7</sup> These experiments were limited by the indirect nature of the connection between the preparation parameters and the final properties of the GIC.

In this work we describe the application of hydrogen doping as a new probe of the relationship between structure and superconductivity in stage-1 KHg-GIC's. In contrast with other experiments relevant to the superconductivity of this compound, exposure to hydrogen yields a result which is reproducible not only among similarly prepared samples, but among stage-1 KHg-GIC's with a wide range of initial properties. Therefore, this technique may properly be used to study the characteristics of stage-1 KHg-GIC's (denoted by  $C_4KHg$  when stoichiometric<sup>8</sup>) without reference to the history of a particular sample. It is remarkable in this context to note that the uniformity of superconducting properties is achieved not by degrading all compounds to the level of the most disordered GIC, but by elevating all of them to the

quality of the best ordered ones.

Generally the stage-1 KHg-GIC has been discussed in conjunction with the corresponding stage-2 compound because of the surprising finding that stage 2 has a higher  $T_c$  than stage 1, despite specific-heat measurements which indicate that stage 2 has a lower density of states at the Fermi level.<sup>9</sup> In this context, a comparison with the potassium-hydride-graphite intercalation compounds should also prove instructive. One reason is that  $C_8KH_{2/3}$  has a triple-intercalate-layer structure<sup>10</sup> similar to that of potassium-mercury GIC's.<sup>8</sup> Also significant as far as superconductivity is concerned is that the  $T_c$  of  $C_8KH_{0.19}$  is 0.22 K,<sup>3</sup> 50% higher than that of its parent compound  $C_8K$ , with a  $T_c$  of 0.15 K.<sup>11</sup>

The hydrogen-doped stage-1 KHg-GIC's described here were prepared in a two-step process, analogous with the preparation of  $C_8KH_x$ .<sup>10</sup> First, three types of stage-1 KHg-GIC's were prepared by the usual two-zone method. Two batches were prepared isothermally at temperatures of 200 and 260°C, respectively, and one was prepared at 200°C with a temperature difference of 4°C. As was described previously,<sup>7</sup> the two batches of GIC's which were prepared at 200°C showed one repeat distance  $I_c$  of  $10.24 \pm 0.03$  Å in (001) x-ray scans, while those prepared at 260°C showed two sets of Bragg peaks, one corresponding to  $I_c = (10.22 \pm 0.03)$  Å, and one to  $I_c = (10.83 \pm 0.03)$  Å.

In order to perform the hydrogen doping, the same samples that were characterized without hydrogen were transferred under vacuum to an ampoule containing 200 mbar of highly purified hydrogen gas. The two isothermally prepared GIC's, which were initially pink, became blue after about 5 min of exposure to hydrogen gas, and then turned a dark purple. The GIC which was prepared with a temperature difference was initially gold, but remained blue-violet indefinitely afterward. The superconducting transitions of all three types of samples were measured inductively (see Fig. 1), while the temperature was monitored by observation of the <sup>3</sup>He vapor pressure.  $T_c$  was determined from the intersection of a tangent drawn to the transition curve with the level upper portion of the trace, and  $\Delta T_c$  was determined by measuring the difference in temperature between the points where the tangent intersected the upper and lower levels of the traces. Subsequent (001) scans showed that the samples' repeat distances were unchanged upon hy-

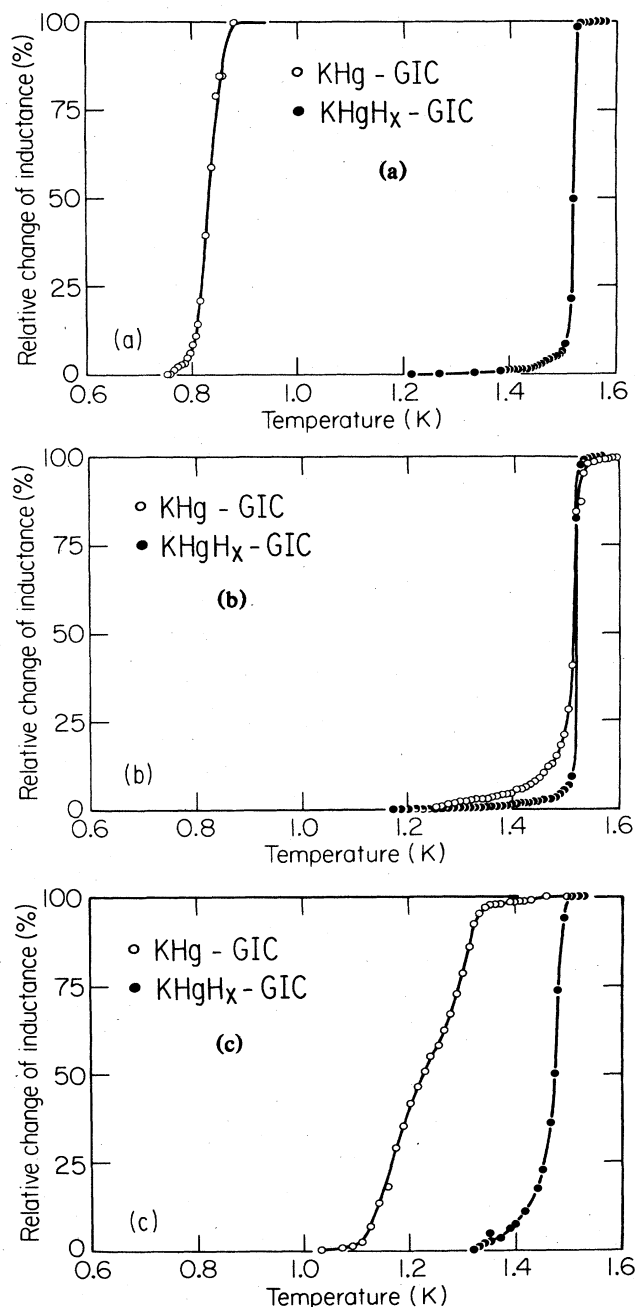


FIG. 1. Effect of hydrogen doping on the superconducting transitions of three types of stage-1  $\text{KHg-GIC}$ 's. (a)  $T_c$  increases from 0.85 to 1.51 K, and  $\Delta T_c$  decreases from 0.035 to 0.011 K. (b)  $T_c$  remains constant at 1.53 K, and  $\Delta T_c$  decreases the same amount as in (a). (c)  $T_c$  increases from 1.32 to 1.49 K, and  $\Delta T_c$  decreases from 0.25 to 0.03 K.

drogen doping, but the effect on the superconductivity was dramatic.

The superconducting transitions of the three types of samples before and after hydrogen doping are shown in Fig. 1. The addition of hydrogen is seen to have produced two effects. One is a marked narrowing of the transition width  $\Delta T_c$  which occurred in all samples measured, especially in the one intercalated at 260°C in which  $\Delta T_c$  went from

$\sim 0.25$  to  $\sim 0.03$  K [Fig. 1(c)]. The other notable effect was the increase of the  $T_c$  of all the samples to  $\sim 1.5$  K, except for the GIC prepared at 200°C, whose initial  $T_c$  of 1.53 K was unchanged by hydrogen uptake [Fig. 1(b)].  $T_c$  increased 80% in the compound prepared with a temperature difference, rising 0.66 K [Fig. 1(a)]. The most significant result overall, though, is that the transitions of all three samples after hydrogen addition strongly resemble one another, whereas before they were quite distinct.

Previous work has correlated the existence of a narrow transition in stage-1  $\text{KHg-GIC}$  samples with the presence of a well-ordered in-plane structure, probably a  $(2 \times 2)R0^\circ$  phase.<sup>6,7</sup> The initially broad transition of the GIC with two repeat distances is then connected with the presence of a second in-plane phase, possibly a  $(\sqrt{3} \times \sqrt{3})R30^\circ$  or a  $(\sqrt{3} \times 2)R(30^\circ, 0^\circ)$  structure,<sup>7</sup> or a disordered structure. Experiments with the application of external pressure to  $\text{KHg-GIC}$ 's have produced a sharpening of the superconducting transition<sup>5</sup> apparently similar to that produced by hydrogen doping. The effect of pressure seems to be the formation of a more homogeneous intercalate structure. The transition narrowing seen in association with hydrogen exposure must also be due to greater uniformity, probably caused by hydrogen diffusion into mercury vacancies associated with disorder. Rapid diffusion of hydrogen atoms is very plausible because of their small size, and is well known to occur in other metallic systems.<sup>12</sup> The total hydrogen uptake may then be limited by the number of available vacant Hg sites, or it may be determined by electronic effects, as in  $\text{KH}_x\text{-GIC}$ 's, where the maximum possible value of  $x = 0.8$  is limited by the finite number of electrons available for transfer to the hydrogen.<sup>13</sup>

Charge transfer to hydrogen is also to be expected in doped stage-1  $\text{KHg-GIC}$  samples because of hydrogen's high electron affinity. The filling of low-lying hydrogen states must remove electrons from intercalate and graphite bands and thus lower the Fermi energy. In the  $\text{KH-GIC}$ 's, the transfer of electrons from potassium to hydrogenic states has already been directly observed using ESR<sup>14</sup> and <sup>13</sup>C NMR.<sup>15</sup> Moreover, recent Shubnikov-de Haas measurements on these compounds show them to have a lower Fermi energy than the parent compound  $\text{C}_8\text{K}$ .<sup>13</sup> To see how the change in electronic occupation might affect the transition temperature of the  $\text{KHg-GIC}$ 's, we can refer to the BCS theory of superconductivity, in which the superconducting transition temperature increases with increasing density of states at the Fermi level according to  $T_c = 1.14\Theta_D \exp[-1/N(E_F)V]$ . Here,  $\Theta_D$  is the Debye temperature,  $N(E_F)$  the density of states at the Fermi level, and  $V$  the electron-phonon coupling matrix element. We see that if the rise in the transition temperature with the uptake of hydrogen is due to a change in the density of states, then the experimentally observed decrease in  $E_F$  must lead to an increase in  $N(E_F)$ . The effect of hydrogen on the three types of samples can then be explained using the schematic density-of-states curves for the normal-state compound shown in Fig. 2.

Figure 2(a) displays the form proposed for the density of states of a  $\text{KHg-GIC}$  with  $T_c$  less than 1.5 K. There are small contributions from the graphite bonding  $\pi$  and antibonding  $\pi^*$  bands, but the density of states is dominated by  $s$ -like and  $p$ -like bands due to potassium and mercury. Note that the Fermi level is above a local maximum in the schematic density of states of the intercalate-derived bands.

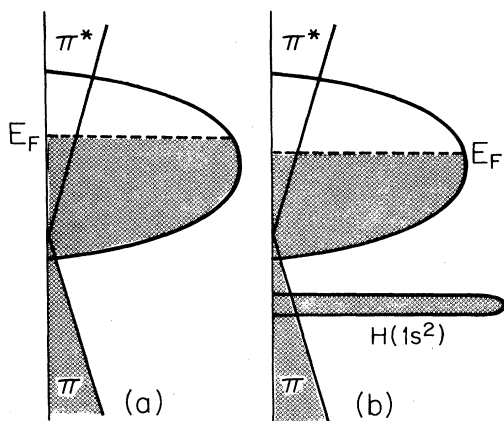


FIG. 2. Schematic model for the density of states in (a) undoped and (b) hydrogenated stage-1 KHg-GIC's. (a)  $N(E_F)$  for an undoped compound with  $T_c$  less than 1.5 K.  $E_F$  lies above the maximum in the density of states in the intercalate bands. (b)  $N(E_F)$  for the hydrogen-doped KHg-GIC. The transfer of electrons from intercalate-derived bands to hydrogen levels has lowered the Fermi level and increased  $N(E_F)$ .

The basic shape of the density of states is consistent with recent electron-energy-loss spectroscopy (EELS) experiments which found strong evidence for the presence of mercury-like and potassium-like contributions to  $N(E_F)$ .<sup>16</sup> Figure 2(b) shows the final configuration for a hydrogenated stage-1 KHg-GIC. Now the Fermi level is lower because of electron transfer from the intercalate and graphite bands into the hydrogen states, but the density of states at the Fermi level is higher. A GIC whose  $T_c$  was unchanged from 1.5 K by hydrogenation must have had its  $N(E_F)$  near that indicated in Fig. 2(b) before doping. Therefore, one concludes that either its hydrogen absorption and associated Fermi-level shift must have been small, or that its Fermi level lies near a broad local maximum in the density of states. Low hydrogen uptake for samples with an undoped  $T_c$  of 1.5 K is consistent with the observation that their color change after hydrogenation was less noticeable than that of the GIC's with a lower undoped  $T_c$ .

Further evidence that the role of hydrogen in stage-1 KHg-GIC's is to accept electrons comes from an examination of the effect of stoichiometry on the superconductivity of KHg alloys. In these compounds,  $T_c$  decreases monotonically with increasing potassium content, from 4.2 K in pure mercury to 0.9 K in KHg itself.<sup>17,18</sup> These data provide strong support for the idea that adding electrons to Hg decreases rather than increases the transition temperature. One can then think of the carbon layers in the potassium-mercury-graphite intercalation compounds as a sink for some of the intercalant electrons, and use this idea to explain why  $T_c$  is higher in stage-1 KHg-GIC's than it is in

the KHg alloy. The hypothesis that hydrogen increases the transition temperature by removing electrons from the intercalate bands is then fully consistent.

The density-of-states model described above could also be extended to treat stage-2 KHg-GIC's. Several different experiments show that the Fermi level in stage 2 is about 0.5 eV lower than in stage 1.<sup>15,16,19</sup> The finding that  $T_c \sim 1.9$  K is higher in stage 2 than in stage 1 may indicate that the same type of density-of-states shift that occurs upon hydrogenation also occurs from stage 1 to stage 2. This conclusion is supported by EELS data which indicates that the density of intercalate states is higher in stage 2.<sup>16</sup> The EELS result is apparently in conflict with the finding from specific-heat measurements that the total  $N(E_F)$  decreases substantially from stage 1 to stage 2.<sup>9</sup> The conflict stems from the fact that for the two results to be consistent one must assign a contribution to  $N(E_F)$  from the graphite  $\pi$  bands which is an order of magnitude larger than that expected for the graphite  $\pi$  bands at this Fermi level.<sup>19</sup> The seeming discrepancy between the density-of-states model and the specific-heat measurements can be resolved by noting that the stage-1 GIC used for the specific-heat measurement was found to be not superconducting down to 0.8 K.<sup>9</sup> Therefore, the upper limit on the transition temperature of the GIC used in the specific-heat experiment is below the lowest  $T_c$  measured for any of the samples described in the present work, which implied that the electronic structure of that compound may well have been different from that of the GIC's described here. If this assertion be correct, then other experiments present a unified picture of the behavior of the density of states in these compounds.

In summary, we have presented the results of a new experiment with many implications for the relationship between electronic structure and superconductivity in the stage-1 KHg-GIC's. The unique property of the experiment is that hydrogen doping produces the same effect on samples with very different initial properties, in contrast with many other methods of studying these compounds. A density-of-states model suggested by the hydrogen-doping results has been described. Extension of the hydrogenation studies to different stages and other compounds should prove to be a great interest.

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