The Effect of Hydrogen Doping on the Superconducting Transition Temperature of KHG-GIC

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Abstract. For stage 1 KHg–GICs, superconducting transition temperatures T_c have been reported in a range from 0.8 K to ~1.5 K, with the variation depending on sample preparation conditions. We show that for all samples, independent of the initial T_c value, the addition of hydrogen results in an increase of T_c to ~1.5 K and a narrowing of the transition width. The implications of this result on the electronic structure are discussed.

Introduction

KHg–GICs exhibit a number of interesting superconducting properties. Among these are a highly anisotropic upper critical field H_{c2}, and the fact that stage 2 samples exhibit a higher T_c value than stage 1 samples, despite a decrease in the total density of states as determined from the electronic specific heat coefficient.[1] In previous work, we showed that the typically observed T_c values of ~0.8 K for stage 1 samples can be increased to 1.5 K by preparing stoichiometric and well-ordered compounds.[2] Still, this value for stage 1 samples is lower than $T_c = 1.9$ K for stage 2. In order to get a better understanding of this unusual T_c variation, Shubnikov-de Haas studies have been carried out on the isostructural KH_x–GICs.[3] For both types of samples, the amount of charge transferred to the graphitic bands could be determined. From these results, it was concluded that for KH_x–GICs a part of the potassium 4s charge is not transferred for stage 1 samples, whereas the charge transfer is complete for stage 2 samples, leading to an ionic intercalate layer K^+H^-. Due to the high electron affinity of hydrogen, KH_x–GICs can only be prepared with a concentration of x up to ~0.8. Similar Shubnikov-de Haas studies have already been performed on KHg–GICs.[4] For KHg–GICs, a larger amount of charge is transferred to the graphitic bands. The charge retained in metal derived bands is higher for stage 1 than for stage 2, and the Fermi energy decreases with increasing stage number. The strong electron affinity of hydrogen opens the possibility of studying the change of the electron distribution in KHg–GICs by adding hydrogen gas to these compounds. This should result in an electron transfer from intercalate and graphite bands into low lying hydrogen levels, thus changing the density of states at the Fermi level and accordingly the superconducting properties. In this paper, we report the results of hydrogen–doping experiments carried out with stage 1 KHg–GICs which had superconducting transition temperatures in the range of 0.8 K to 1.53 K prior to the doping.

Experimental Details

The stage 1 KHg–GICs used for the hydrogen doping experiments, were prepared as described previously.[2] After the superconducting and structural parameters were determined for the pristine KHg–GICs,the samples were then transferred under vacuum into a new sample tube, which was filled with ~20 mbar of ^{4}He exchange gas for the T_c measurements and in addition with ~200 mbar of high purity H_2 gas from a hydrogen purifier. The initial reaction of the added H_2 gas with the GIC was quite rapid. After ~1 min the surface of the sample changed from a light pink to a darker pink with a bluish shade. For samples with an initial T_c value of 0.8 K, the color changed to a mixture of blue and violet. No further obvious change of the sample occurred and it was sealed off from the H_2 reservoir typically after ~10 min, although some samples were exposed to the hydrogen reservoir for up to 2 hrs. For all samples, the repeat distance was determined to be $(10.24 + 0.02)$Å, using $(00l)$x-ray diffraction. This repeat distance remained unchanged by the hydrogen doping.

Results and Discussion

Figure 1 shows the effect of doping stage 1 KHg–GICs with hydrogen on the superconducting transition temperature T_c and the width of the transition. For the different samples used, the addition of hydrogen has two clearly distinguishable effects: a) for all samples with T_c values initially below ~1.5 K, T_c is increased to ~1.5 K. Fig. 1a shows the increase in T_c for a sample with an initial T_c value of 0.85 K. b) For all samples, independent of the initial T_c value, the transition width ΔT_c narrows considerably (Fig. 1a and b). This narrowing was very dramatic for a sample with an initial T_c value of 1.32 K. For this sample, ΔT_c decreased from several tenths of a degree at $T_c = 1.32$ K to a value of ΔT_c of ~ 0.03 K. For the other samples, the already sharp transition further decreases to an extremely narrow

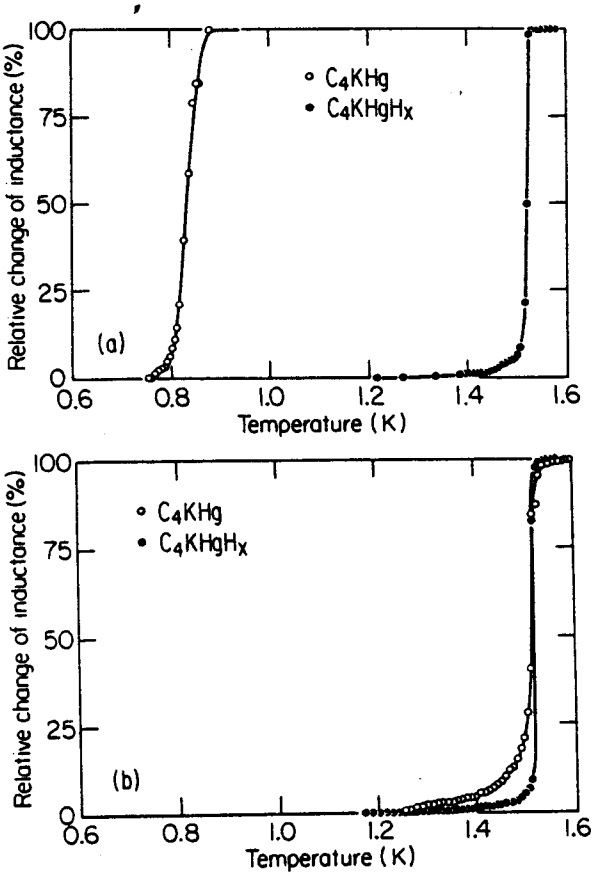

Figure 1: The effect of doping stage 1 KHg–GIC with hydrogen on the superconducting transition temperature T_c for samples with an initial value of: (a) $T_c = 0.85$ K and (b) $T_c = 1.53$ K.

ΔT_c of ~ 0.011 K (Fig. 1a and b). We suggest that this behavior is caused by two different effects of the hydrogen on the KHg–GIC samples. As we have shown in previous experiments,[2] the occurrence of a narrow superconducting transition is connected to homogeneous samples, most likely with a well ordered (2×2)R0° in–plane structure. We therefore suggest that the addition of hydrogen, which is highly mobile, increases the homogeneity of the KHg–GIC by filling vacant mercury sites and thus stabilizing the (2×2)R0° in–plane structure. The second effect is that the hydrogen, as a strong electron acceptor, changes the electronic structure due to the presence of low-lying hydrogen states, which are filled with electrons from the conduction band. This filling of the low-lying hydrogen states changes E_F and the density of states at the Fermi level. According to the BCS theory, an increase in T_c can be obtained by a corresponding increase in $N(E_F)$. We therefore suggest, that the effect of hydrogen doping can be explained usingthe following schematic model for the density of states curve (Fig. 2). In the undoped KHg–samples, conduction electrons derived from intercalate bands and graphite π bands are simultaneously present at the Fermi level, with the intercalate states filled to an energy that is above the maximum in the density of states curve. The addition of hydrogen then

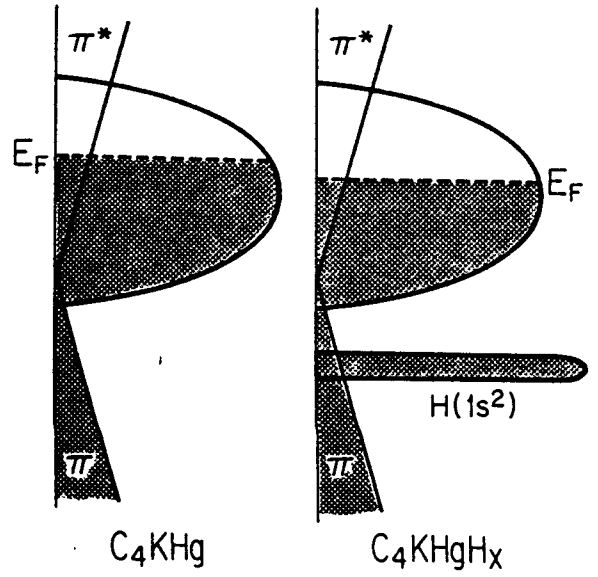

Figure 2: Schematic model for the density of states curve.

leads to an increase in T_c, corresponding to a higher $N(E_F)$, since a part of the intercalate and graphitic electrons now occupy low lying hydrogen states. A similar picture may be used to explain the T_c variation observed in stage 1 and stage 2 KHg–GICs. In these compounds, T_c also increases, while E_F, as determined from the Shubnikov–de Haas experiments, decreases.[4] This is in agreement with recent EELS observations that the Fermi energy is lower in stage 2 KHg–GICs than in stage 1, whereas the density of states in the intercalate-derived bands is increased.[5]

Acknowledgments

The authors G.R., A.C., N.C.Y. and G.D. gratefully acknowledge support by AFOSR #F49620–83–C–0011 and T.E. by DOE Grant #DE–AC02–83ER45041 and a grant from the Japanese Ministry of Education. P.T. gratefully acknowledges support by the NSF.

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