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 Tc 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 Tc value, the addition of hydrogen results in an increase of Tc 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 Hc2, and the fact that stage 2 samples exhibit a higher Tc value than stage 1 samples, despite a decrease in the total density of states as determined from the electronic specific heat coefficient. In previous work, we showed that the typically observed Tc values of ~0.8 K for stage 1 samples can be increased to 1.5 K by preparing stoichiometric and well-ordered compounds. Still, this value for stage 1 samples is lower than Tc = 1.9 K for stage 2. In order to get a better understanding of this unusual Tc variation, Shubnikov-de Haas studies have been carried out on the isostructural KHg–GICs. 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 KHg–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, KHg–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. 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. 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 4He exchange gas for the Tc measurements and in addition with ~200 mbar of high purity H2 gas from a hydrogen purifier. The initial reaction of the added H2 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 Tc 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 H2 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 Tc 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 Tc values initially below ~1.5 K, Tc is increased to ~1.5 K. Fig. 1a shows the increase in Tc for a sample with an initial Tc value of 0.85 K. b) For all samples, independent of the initial Tc value, the transition width ΔTc narrows considerably (Fig. 1a and b). This narrowing was very dramatic for a sample with an initial Tc value of 1.32 K. For this sample, ΔTc decreased from several tenths of a degree at Tc = 1.32 K to a value of ΔTc of ~0.03 K. For the other samples, the already sharp transition further decreases to an extremely narrow...
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. 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.  

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