Electrical Properties of KH–Graphite Ternary Compounds: $C_{4n}KH_x$

T. Enoki
Institute for Molecular Science, Okazaki 444, Japan

and

N.C. Yeh, G. Roth, G. Dresselhaus and M.S. Dresselhaus
Massachusetts Institute of Technology, Cambridge, MA 02139

Abstract. Potassium–hydrogen–graphite ternary compounds (KH_z–GIC) are donor type intercalation compounds with an approximately ionic intercalant $K^+H_x^-$. We report temperature dependent Shubnikov–de Haas results on stage–1, 2, 4 KH_z–GICs and stage–1 KD_z–GICs. The presence of hydrogen with a large electron affinity induces a charge transfer from K to H, which gives different electronic properties from those of C_8K.

Introduction

The ternary compounds potassium–hydrogen graphite intercalation compounds (GICs) are donor type intercalation compounds with an approximately ionic intercalant $K^+H_x^-$. Transition metal hydrides such as PdH_x are metallic alloys because of the intimate interaction between the transition metal conduction electrons and the hydrogen electrons, while alkali metal hydrides such as K^+H^- are ionic insulators where hydride anions H^- with localized character are stabilized. In the KH_z–GICs, hydrogen atoms interact directly with the neighboring potassium atoms so that the hydrogen layer is surrounded by a metallic medium, the properties of which are associated with the presence of graphitic π and K 4*s* electrons. The conduction electrons are largely screened from the hydrogen layer by the surrounding potassium layers in the KH_z–GICs. Thus the electrons in the intercalate layers of the KH_z–GICs are more metallic than in pristine KH but more localized than for alkali metal hydrides, thus giving rise to novel electronic and structural properties in the KH_z–GICs. In this report, Shubnikov–de Haas (SdH) results for KH_z–GICs including their temperature dependence are presented. These results are compared with those of the KHg_x–GICs which are isostructural to the KH_z–GICs and have a metallic intercalant KHg.

Results and Discussion

The samples of $C_{4n}KH_x$ were prepared from HOPG pieces with a typical dimension of $6 \times 2.5 \times 0.1 mm^3$ using a direct KH intercalation method. The intercalation temperatures were 410 to 380°C and 210 to 200°C for the stage–1 and –2 compounds, respectively.

For the Shubnikov–de Haas (SdH) studies, the magnetoresistance was measured in the field range up to 23T at liquid helium temperatures. Some typical magnetoresistance traces are shown in Fig. 1 for the stage–1, 2 and 4 KH_z–GICs. The magnetoresistance of the stage–1 KH_z–GICs shows three SdH frequencies (ν_α = 30T , ν_β = 110T and ν_γ = 650T), while the three frequencies of the stage–2 KH_z–GICs are (ν_α = 41T, ν_β = 276T and ν_γ = 1510T). The four SdH frequencies for the stage–4 KH–GIC (which has I_c = 18.18Å from (00*l*) X–ray diffraction spectra) were determined to be ν_α = 32T, ν_β = 164T, ν_γ = 309T and ν_δ = 461T. It is found that the calculated frequencies using the dilute–limit model are in an excellent agreement with the observed frequencies in the stage–4 KH_z–GIC. (See Table 1.) The dilute–limit model does not work as well for the stage–1 and –2 KH_z–GIC samples.

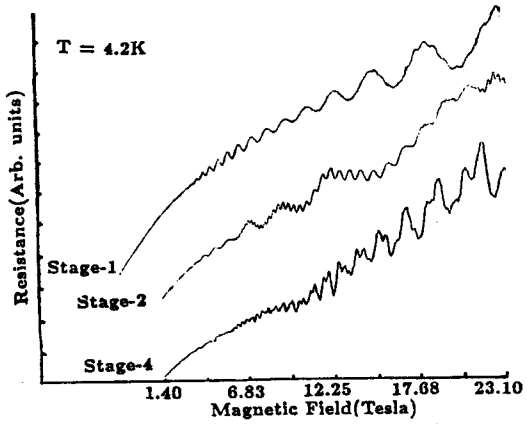

Figure 1: Observed magnetoresistance of stage 1, 2 and 4 KH_z–GICs.

Table 1: Comparison between calculated and observed SdH frequencies using 3D dilute–limit model for stage–4 KH_x–GIC.

$\nu_{calculated}$(Tesla)	$\nu_{observed}$(Tesla)
461	461
419	–
309	309
161	164
–	32

The angular dependence suggests that the oscillations are associated with cylindrical Fermi surfaces of graphitic bands. The electronic structures are analyzed with a phenomenological model based on the graphitic bands given by the following equation:[1]

$$A^e_{max} = (4\pi/3a_0{}^2\gamma_0^2)[E_3 - E_f][E_2 - E_f]/(1+2\gamma_4/\gamma_0)^2$$

where $\gamma_0 = 3.1$ eV for the overlap energy of neighboring atoms in a single graphite layer plane, $\gamma_1 = 0.39$ eV for the overlap of orbitals associated with carbon atoms located one above the other in adjacent graphitic layer planes, and a = 2.46Å. Table 2 summarizes the parameters for the electronic structures of the stage–1 and –2 KH_x–GICs. In the case of the stage–2 KH_x–GIC the calculated number of electrons donated to each carbon atom $f_C = 0.038$ suggests complete charge transfer $f_K = 1$ from a potassium atom for $C_8KH_x(x \sim 0.8)$[2] assuming that each hydrogen atom grabs one electron from the potassium band due to the large electron affinity of hydrogen. This is consistent with the experimental low temperature specific heat results which give $f_C = 0.044$ for $C_8KH_{0.65}$,[3] since the smaller amount of hydrogen uptake requires the transfer of fewer electrons from the potassium, and more is then available for the graphite layers. A comparison between the present Shubnikov–de Haas results and the specific heat results reveals that the increase in hydrogen concentration in the intercalate layers of the stage–2 C_8KH_x compounds reduces the number of donated electrons accommodated in the graphitic bands. The absence of superconductivity[4] in the stage–2 compound can be explained by the absence of K 4*s* electrons, since superconductivity in donor–GICs requires the presence of both graphitic and *s* electrons.[5] For the stage–1 KH_x–GIC, the number of donated electrons to each carbon atom is estimated to be $f_C = 0.016$. These evaluations of the charge transfer to the carbon and hydrogen atoms suggest incomplete charge transfer from potassium $f_K = 0.87$ for the stage–1 compound if x=0.8 is assumed[2,6] in C_4KH_x.

The temperature dependence (from 1.3 K to 20 K) of the SdH amplitudes was obtained for both stage–1 KH_x–GICs and KD_x–GICs to determine the effective masses for these samples. Both the stage–1 KH_x–GIC and stage–1 KD_x–GIC samples exhibit the same basic electronic properties and their effective masses were determined to be $0.046m_0$ for the ν_α = 30T period and $0.23m_0$ for the ν_β = 110T period, where m_0 = free electron mass (see Fig. 2).

Table 2: Summary of the charge transfer f_C and f_K values and SdH frequencies ν_{max} in various samples.

	f_C (e^-/C)	f_K (e^-/K)	ν_{max} (SdH in T)
$C_4KH_{0.8}$	0.016	0.87	650
$C_8KH_{0.8}$	0.038	1.0	1510
C_8K[a]	0.074	0.60	2870
$C_{24}K$[b]	0.042	1.0	439
C_4KHg_x[c]	0.063	~ 1	2490
C_8KHg_x[c]	0.025	~ 1	1490

[a]S. Tanuma, H. Suematsu, K. Higuchi, R. Inada, and Y. Onuki, *Proceedings of the Conference on the Application of High Magnetic Fields in Semiconducter Physics*, ed. J.F. Ryan. (Oxford; Clarendon Press, 1978), p.85.
[b]G. Dresselhaus and S.Y. Leung, *Solid State Commun.* 35, 819 (1981).
[c]G. Timp, T.C. Chieu, P. Dresselhaus and G. Dresselhaus, *Phys. Rev.* B29, 6940 (1984).

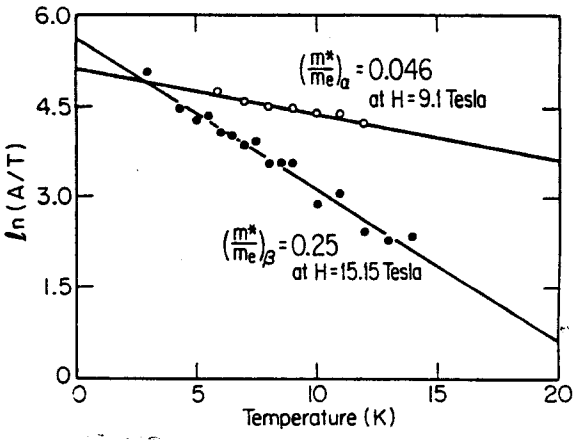

Figure 2: Temperature dependence of the amplitude of two periods for the stage–4 KH_x–GIC. The lines are for the indicated effective masses.

Acknowledgments

The MIT work is supported by AFOSR #F49620–83–C–0011.

References

[1] M.S. Dresselhaus and G. Dresselhaus, *Advances in Physics* 30, 139 (1981).

[2] D. Guérard, C. Takoudjou and F. Rousseaux, *Synthetic Metals* 7, 43 (1983).

[3] T. Enoki, M. Sano and H. Inokuchi, to be published.

[4] M. Sano, H. Inokuchi, M. Kobayashi, S. Kaneiwa and I. Tsujikawa, *J. Chem. Phys.* 2, 3840 (1980).

[5] R. Al–Jishi, *Phys. Rev.* B28, 112 (1982).

[6] N.C. Yeh, T. Enoki, L. Salamanca–Riba and G. Dresselhaus, Extended Abstract of this conference (1985).