Structural Properties and Magnetic Susceptibility of Potassium-Hydrogen Intercalated Graphite

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Abstract. The synthesis, structural determination and magnetic properties of KH_x-GICs are presented. Stage 1, 2, 4 of KH_x-GICs and stage 1, 2 of KD_x-GICs were prepared and characterized using (00l) X-ray diffraction, high resolution transmission electron microscopy (TEM) and Raman scattering. The temperature dependence of the magnetic susceptibility for both stage-1 and stage-2 KH_x-GICs was also obtained. Values for the electronic specific heat constant γ for both stage-1 and stage-2 KH_x-GICs and KD_x-GICs estimated from susceptibility measurements are also consistent with the Shubnikov-de Haas results.

Introduction

The intercalation mechanism in the ternary KH-graphite intercalation compounds (KH_x-GICs) was found to be similar to that in KHg_x-GICs in that the process involves an initial intercalation of K followed by the subsequent intercalation of the hydrogen or mercury. Stage 1, 2, 4 of KH_x-GICs and stage 1, 2 of KD_x-GICs were prepared and characterized using (00l) X-ray diffraction, high resolution transmission electron microscopy (TEM) and Raman scattering. The temperature dependence of the magnetic susceptibility for $\vec{H} \parallel c$-axis ($\chi_\parallel$) of both stage-1 and stage-2 KH_x-GICs was also obtained using a SQUID magnetometer and was found to be remarkably different from those in K-GICs.[1] The specific heat constant γ in stage-2 KH_x-GICs estimated from the present susceptibility measurements was found to be in good agreement with the γ obtained from the low temperature heat capacity experiment.[2] The γ values for both stage-1 and stage-2 KH_x-GICs and KD_x-GICs estimated from susceptibility measurements are also consistent with Shubnikov-de Haas results on similarly prepared samples.[3]

Intercalation Mechanism

Stage 1 KH_x-GICs and KD_x-GICs can only be obtained by the direct KH or KD-intercalation method. Both intercalates have about the same repeat distances as measured by X-ray diffraction and TEM. After heating graphite with KH or KD powders in a sealed ampoule for a few hours at constant temperature (350°C < T < 420°C), the samples became golden in color, indicating the formation of stage-1 K-GICs. The samples were taken out of the furnace after 1 or 2 days and studied by (00l)X-ray diffraction. They showed admixtures of stage-1 and -2 KH_x-GICs. (Sometimes at a lower intercalation temperature, *e.g.* 320°C, small traces of stage-1 K-GIC were also found in these samples.)[5] Though the volume fraction of stage-2 KH_x-GICs decreased as a function of time, some stage-2 remained in the sample for temperatures up to 420°C and intercalation times up to 18 days. The final equilibrium state consisting of both stage-1 (about 80 % *to* 90 %) and stage-2 KH_x-GICs may be due to the starting material (C_8K), which can easily form stage-2 KH_x-GICs under exposure to hydrogen gas.[2] In contrast to the usual synthesis of stage-2 KH_x-GICs by a two-step chemisoption method,[2] we used the direct KH or KD intercalation method[5] and found a remarkably different intercalation mechanism showing the preferred starting material for direct synthesis to be a stage-2 K-GIC instead of a stage-1 K-GIC (see Fig. 1). To gain further insight into the intercalation mechanism, *in situ* experiments on these samples are in progress.

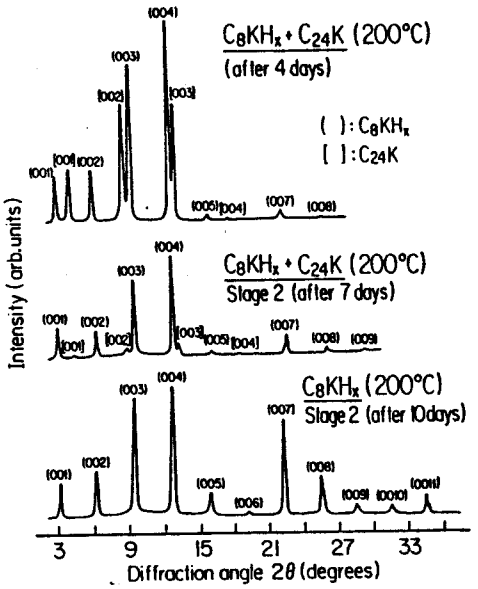

Figure 1: (00l) X-ray traces for various times in the intercalation sequence of KH_x-GICs (see text).

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Raman Scattering

As reported previously,[5] the stage–1 KH_x–GICs have a higher E_{2g_2} Raman shift (1596 ± 3 cm^{-1}) than the stage–1 binary alkali metal–GICs and ternary KHg_x–GICs due to the strong electron affinity of the hydrogen atoms. The lineshape for stage–1 KH_x–GICs is Lorentzian which indicates that no strong coupling to continuum modes occurs such as is observed by the Breit–Wigner lineshape for the stage–1 K–GIC. In contrast, the stage–2 KH_x–GICs exhibit a Raman shift (1599 ± 3 cm^{-1}) close to the usual Raman shift for stage–2 donor GICs. The stage–1 KD_x–GICs are reported here to have the same Raman shift as that in KH_x–GICs but with a larger linewidth. The Raman shifts of a stage–4 KH_x–GIC were also studied and found to be 1581 ± 3 cm^{-1} and 1612 ± 3 cm^{-1}) for the interior and bounding graphite layer modes, respectively.

Magnetic Susceptibility

The temperature dependence of the magnetic susceptibility of both stage–1 and stage–2 KH_x–GICs with magnetic field parallel to the c–axis were obtained using a SQUID magnetometer. The results are fit by a functional form $(\chi_\parallel)_{total} = a_1 + a_2/(T + a_3)$ (see Fig. 2), where $a_1 > 0$, $a_2 < 0$ and $a_3 > 0$ (see Table 1). Since $\chi_{total} = \chi_{Pauli} + \chi_{core} + \chi_{orbital}$, the constant term a_1 is equal to the sum of χ_{Pauli} and χ_{core} contributions. Thus only $\chi_{orbital}$ contributes to the temperature dependent term. The a_1 value for the stage–1 KH_x–GICs is found to be 0.834×10^{-6} emu/gram $C_4KH_{0.8}$ and 0.988×10^{-6} emu/gram $C_8KH_{0.8}$ for the stage–2 KH_x–GICs. The χ_{core} values were calculated and are listed in Table 1. Since $\chi_{Pauli} = 3\mu_B^2\gamma/(\pi^2 k_B^2)$, if the electron–phonon enhancement in χ_{Pauli} is neglected, the specific heat constant γ evaluated by subtracting the core contribution from the a_1 values gives $\gamma = 0.33$mJ/(K^{2}mole) for stage 1 and $\gamma = 0.47$ mJ/(K^{2}mole) for stage–2 KH_x–GICs. Comparing this to the heat capacity measurements on the stage–2 KH_x–GICs[2] which give $\gamma = 0.46$mJ/(K^{2}mole) if $x = 0.67$ in C_8KH_x, and $\gamma = 0.4$ mJ/(K^{2}mole) if one extrapolates to $x = 0.8$ in the γ *vs.* x plot[2] assuming γ is linear with x. Excellent agreement is thus found between the present susceptibility measurements and the heat capacity experiments. The small deviation in the γ values if $x = 0.8$ is adopted may be due to our neglect of the electron–phonon enhancement in γ. We further note an unusual result $\gamma_{stage-1} < \gamma_{stage-2}$, which can be explained using the carrier densities per carbon atom obtained from Shubnikov–de Haas experiments.[3] Since the largest frequencies are $\nu_{max} = 650$ tesla for stage–1 and $\nu_{max} = 1510$ tesla for stage–2 KH_x–GICs, the estimated numbers of electrons per carbon atom are $(f_C)_{stage-1} = 0.016$ and $(f_C)_{stage-2} = 0.038$ if the (2×2)R0° in–plane structure is assumed in both stages. Thus it is not surprising to find a smaller γ in stage–1 samples than in stage–2 samples.

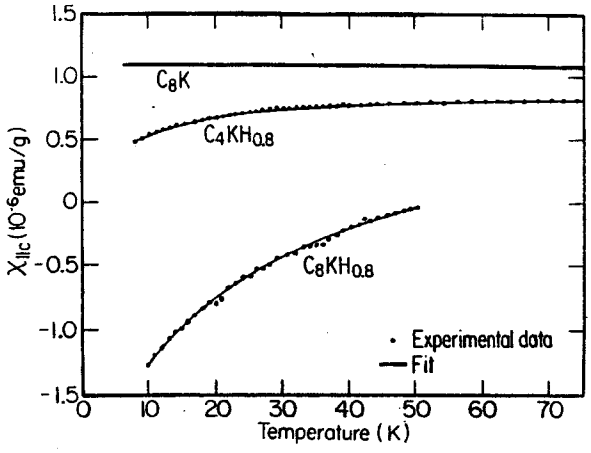

Figure 2: Temperature dependence of the susceptibility for stage–1 C_8K, stage–1 KH_x–GIC and stage–2 KH_x–GIC. The solid lines are fits of experimental points to the model.

Table 1: Summary of the χ and γ values in various samples

	$C_4KH_{0.8}$	$C_8KH_{0.8}$	C_8K	$C_{24}K$	HOPG[a]
a_1[b]	0.834	0.988	–	–	–
a_2[b]	-6.00	-74.56	–	–	–
a_3[b]	6.11	23.77	–	–	–
$\chi_{\parallel total}$[b]	[c]	[c]	1.02[d]	1.50[d]	-21.1[d]
χ_{core}[b]	-2.13	-3.71	-0.38[d]	-0.39[d]	-0.4[d]
χ_{Pauli}[b]	2.96	4.65	0.64[d]	0.25[d]	0.016[d]
γ[e]	0.33[f]	0.47[f]	0.697[g]	0.241[g]	0.03[g,h]

[a] See Ref. 7.
[b] All in units of 10^{-6} emu/g.
[c] $a_1 + a_2/(T + a_3)$
[d] See Ref. 1.
[e] Units of mJ/(K^{2}mole).
[f] Neglecting electron–phonon enhancement.
[g] U. Mizutani, T. Kondow and T.B. Massalski, *Phys. Rev.* B17, 3165 (1978).
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Of particular interest is the remarkably different temperature dependence of χ in KH_x–GICs relative to that for both stage–1 and stage–2 K–GICs, for which χ is paramagnetic and nearly temperature independent. In contrast, the temperature dependence of χ for KH_x–GICs is similar to that for pristine graphite though the magnitude is much smaller.[5,8] The decrease of the γ values in the KH_x–GICs relative to the K–GICs is attributed to the reduction in the mobile free electron density in the graphite layers due to the strong electron affinity of the hydrogen. We also conclude that it is not likely that paramagnetic H_2^- species are present in the KH_x–GICs because of the large paramagnetic contribution they would make at low temperature (about 54.5×10^{-6} emu/gram $C_8KH_{0.8}$ for the temperature range from $6K$ to $100K$ if all the hydrogen were in the H_2^- form).

Acknowledgments

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