

Instabilities of intercalated graphite structures - EPR oscillations

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Summary

EPR studies of HOPG-potassium intercalated (first stage) are described for three samples: C_8K , C_8K_{ex} (with excess of potassium) and C_6KO_y with $y < 0.2$ (C_4KO_x potassium double layer + C_8K , $x < 0.2$).

EPR of pristine HOPG and C_8K (stoichiometric) consists of one Dysonian line whereas C_8K_{ex} and C_6KO_y exhibit complex spectra. The analysis of these spectra allowed to decompose them into Dysonian and Lorentzian lines and to estimate their relative contributions. The temperature dependence of Dysonian component in C_8K_{ex} spectrum is the same as the EPR spectrum temperature dependence of stoichiometric C_8K . The second component, the Lorentzian one is due to localized electrons. This component follows Curie law on cooling. On lowering temperature, a very strong oscillations in the EPR spectrum have been observed in C_8K_{ex} . The temperature at which the oscillations start, the temperature range and the strength of these oscillations seem to occur at random. Such behavior can be related to local instability of stoichiometry x in C_xK samples. Redistribution of potassium ions between stiffened graphitic planes appears at low temperature also in two phase C_6KO_y system (C_4KO_x potassium double layer for $x < 0.2$, and C_8K). It confirms that alkali redistribution modulates conducting band and leads to magnetic non-resonant fluctuations

Introduction

Dense potassium-graphite systems can be obtained in two ways: using the high pressure or by reaction between graphite and liquid potassium containing small amount of oxygen. Formation of dense phases in K-graphite system results in higher critical temperature of superconducting transition T_c . For pressure induced C_3K , the transition to superconducting state occurs at $T_c = 3$ K [1]. Lower potassium concentrations as C_6K ($T_c = 1.5$ K) with $\sqrt{3} \times \sqrt{3}$ superlattice ordering, has close to complete charge transfer as LiC_6 [2].

The small oxygen/potassium ratio in K-graphite systems (reaction with liquid potassium) allow the superimposition of two potassium layers in graphitic interlayer space in C_4KO_x ($x < 0.2$). Such graphite intercalation compounds (GICs) are generally

accepted to be unstable during the cooling from reaction temperature to room temperature [3].

In this paper we report on EPR studies of HOPG (highly oriented pyrolytic graphite) K-intercalated (first stage) for three samples: C_8K , C_8K_{ex} (with excess of potassium) and C_6KO_y (mixture of C_4KO_x potassium double layer $x < 0.2$ and C_8K).

The model of paramagnetic centers in fullerene and intercalated fullerite, based on the analogy of fullerene and graphite was given by Stankowski et al. [4]. Kinetics of intercalation of fullerite C_{60} has shown that ions (or atoms) of potassium easily occupy octahedral voids in fcc fullerite structure during the doping process at 200 °C [5]. At room temperature (or lower), redistribution of intercalate occurs [6,7]. Potassium ions diffuse to tetrahedral, smaller than octahedral voids, to which the access is more laborious. Such redistribution leads to the occurrence of superconductivity. Under certain circumstances even two critical temperatures of superconducting transition can be detected [7,8].

In GICs there are also different critical temperatures of superconducting transition related to different content of intercalate [1,9]. The study of alkali metal intercalated graphite can enrich our understanding of intercalated fullerite as well as our understanding of superconductivity in both systems.

Experimental

C_8K and C_8K_{ex}

Platelets of HOPG (from Union Carbide) were carefully degassed at 370 °C down to 10^{-6} mbar, and then allowed to react for one week with excess of potassium vapor.

Two kinds of samples were obtained: stoichiometric C_8K and C_8K_{ex} containing an excess of metallic potassium mostly on the edges of the platelets. C_8K samples were obtained using the conventional two bulb method with: $T_K = 185$ °C and $T_{HOPG} = 215$ °C. C_8K_{ex} samples were prepared by condensation of K vapor on the edges of the C_8K platelets using $T_K > T_{HOPG} = 215$ °C.

C_6KO_y

Potassium was mixed with 4 % (atomic percentage) of KO_2 in an evacuated Pyrex tube and heated at 200 °C for homogenization. Then HOPG platelets were dipped in the liquid phase of oxygenated K for one month at 200 °C in order to allow the reaction. The Pyrex tube was kept vertically in the furnace in order to avoid the segregation between the samples and the liquid reacting phase. The reaction tube (diameter 8 mm) was then put in a larger sealed tube (diameter 12 mm) and evacuated at 10^{-5} mbar. The excess of liquid oxygenated potassium was extracted from the intercalated samples by heating the sample at 250 °C, while the other end of the tube was kept at $T=150$ °C to allow condensation of the excess of reactant. This process was continued until the characteristic “reddish” golden color disappeared in order to avoid a fully desintercalation. The C_6KO_y composition of the samples was determined by measuring (in the glove box) the weight uptake.

All the samples were transferred under vacuum in the glove box into quartz capillaries and sealed for X-ray (diameter 1 mm) and for EPR measurements (diameter 5 mm).

X-ray experiments, with the c axis in the plane of the incident and diffracted beam and slow rotation of the sample ($4^\circ/h$), were performed in the reflection mode (platelet rotation from $\theta = 0^\circ$ to $\theta = 30^\circ$) and in the transmission mode (platelet rotation from

$\theta = 0^\circ$ to $\theta = 30^\circ$) in order to obtain $00l$ and hkl diffraction patterns, respectively. In the experiment position sensitive detector (INEL CPS 120) at $\lambda = 0.70926 \text{ \AA}$ was used. For C_8K_{ex} sample the X-ray diffraction experiments were performed in 77 - 300 K temperature range.

Results and discussion

X-ray of C_8K_{ex}

The $00l$ diffractogram of C_8K (Fig. 1a) is typical of a first stage phase (identity period $I_c = 5.35 \text{ \AA}$). In C_8K_{ex} additional lines of metallic potassium are observed (Fig. 1b). The 2×2 R 0° 2D structure, typical of potassium bidimensional arrangement in C_8K , was found on the C_8K and C_8K_{ex} hkl diffractograms (Fig. 2a and 2b). In the C_8K_{ex} sample, no structural changes were observed from 300 K to 77 K, both, in the 2D structure of potassium superlattice and in the $\alpha\beta\gamma\delta$ (A represents the graphitic plane) stacking of potassium layers [10] similarly to C_8K graphite intercalation compound.

X-ray of C_6KO_y

The $00l$ diffractogram of C_6KO_y indicates the presence of two first stage phases: binary C_8K ($I_c = 5.33 \text{ \AA}$) and a ternary phase with $I_c = 8.64 \text{ \AA}$ (Fig. 1). The formula of the latter phase is C_4KO_x ($x < 0.2$) as previously reported by Herold et al. [2]. This phase was formed by the reaction of slightly oxygenated potassium. The intercalated sheets contain two superimposed potassium layers sandwiching the oxide anions in the central plane.

On hkl diffraction pattern (Fig. 2) two alkali metal 2D structures were identified: 2×2 superlattice typical of the first stage C_8K and $\sqrt{3} \times \sqrt{3}$ 2D lattice attributed to the in-plane arrangement of K double layer in C_4KO_x dense phase. The stacking of the potassium layers observed in first stage C_8K is typically $\alpha\beta\gamma\delta$ as $c = 4I_c$ [10].

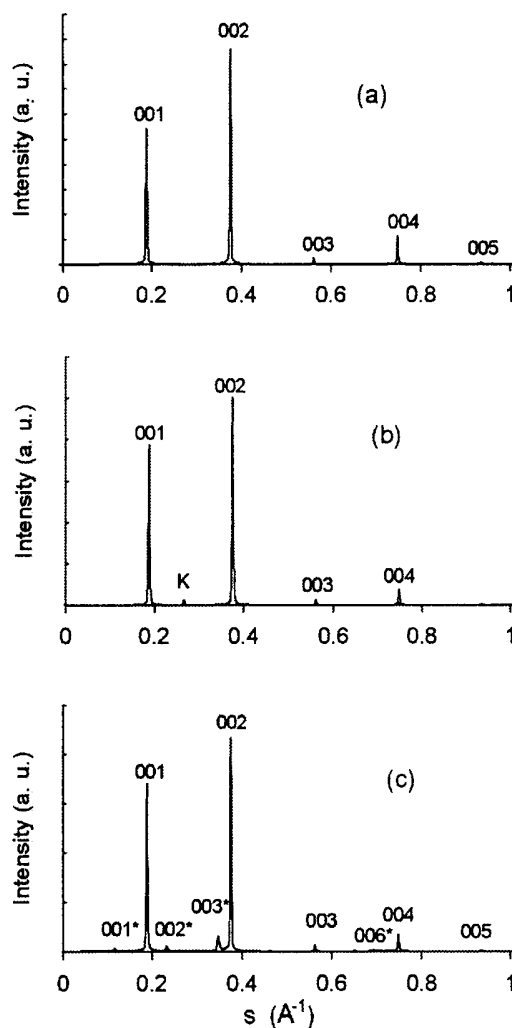


Fig. 1 $00l$ diffractograms of (a) pure C_8K first stage ($I_c=5.33 \text{ \AA}$), (b) C_8K_{ex} sample (lines of pure bcc potassium are labeled by K), (c) C_6KO_y sample ($00l^*$ lines belong to the dense phase C_4KO_x in which $I_c=8.64 \text{ \AA}$). $00l$ lines of pure C_8K first stage binary phase appear in each sample.

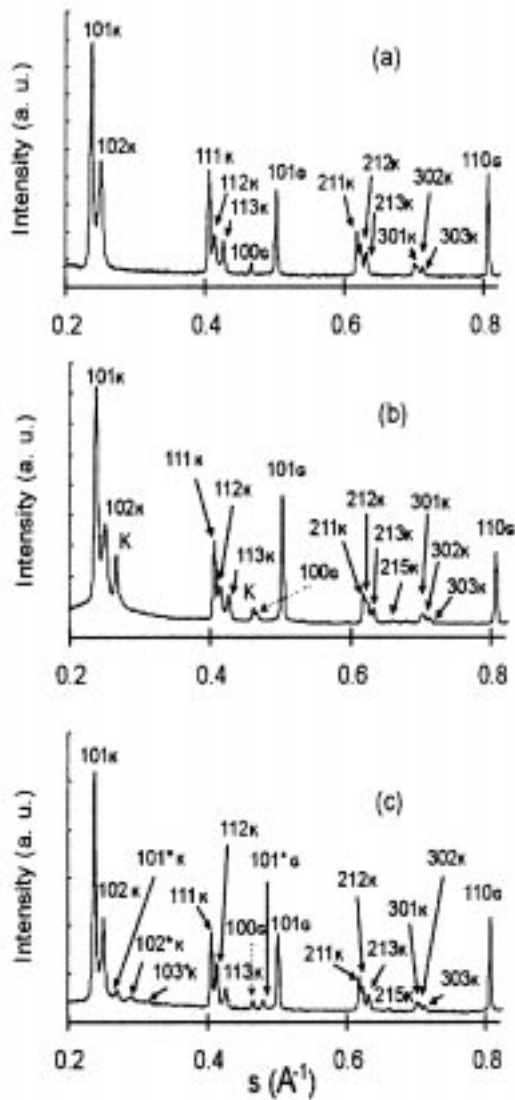


Fig. 2 hkl diffractograms of (a) pure first stage C_8K ($I_c=5.33 \text{ \AA}$) (b) C_8K_{ex} , (c) C_6KO_y sample. Lines of bcc potassium are labeled by K. hkl_k lines belong to the 2×2 potassium superlattice of the pure C_8K phase and are indexed in a $\alpha\beta\alpha\gamma\alpha\delta$ stacking, $I_c=8.33 \text{ \AA}=c/4$. hkl^* lines belong to the $\sqrt{3} \times \sqrt{3}$ potassium superlattice of the dense C_4KO_x first stage and are indexed with $c=2I_c$ ($\alpha\beta\alpha\alpha\beta$ stacking, $I_c=8.64 \text{ \AA}$). hkl_G and hkl^*_G lines belong to the graphite host lattice with $A/A/A$ stacking (l represents the intercalated layers) respectively in first stage C_8K ($I_c=5.33 \text{ \AA}$) and in the dense first stage C_4KO_x ($I_c=8.64 \text{ \AA}$).

The stacking of the double layer of potassium could be $\alpha\beta\alpha\alpha$ as the value $c = 2I_c$ enables to index the $10l$ lines belonging to the $\sqrt{3}\sqrt{3}$ 2D superstructure.

EPR

The EPR spectra of pristine HOPG and stoichiometric C_8K are the same as those reported previously [11]. The EPR spectrum of C_8K (stoichiometric) consists of one Dysonian line whereas that of C_8K_{ex} and C_6KO_y are a complex spectra. The analysis of these spectra, based on Feher, Lauginie or Koder method [11-13] allow to decompose them into Dysonian

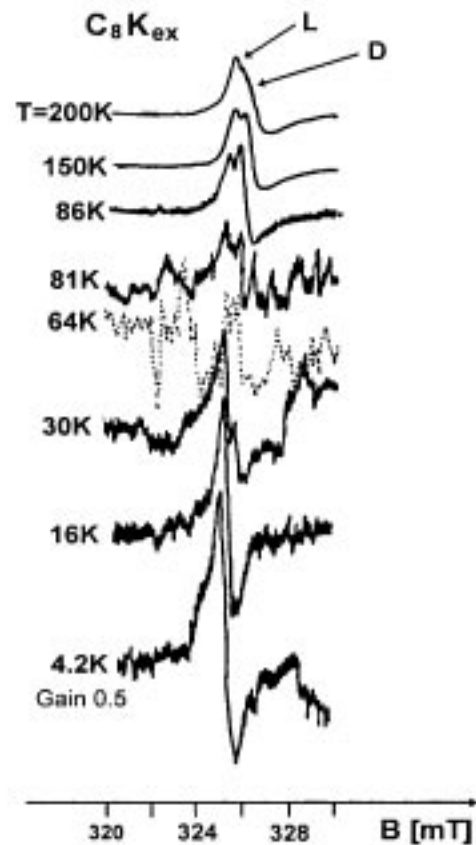


Fig. 3 EPR spectra of C_8K_{ex} with strong oscillations below 90K. L and D mark Lorentzian and Dysonian components, respectively.

and Lorentzian lines and to estimate their relative contributions. For C_8K_{ex} Dysonian line at $g_{\perp} = 2.0032$ with $g_{\perp} - g_0 = 9 \times 10^{-4}$ is typical for stoichiometric C_8K [11] ($g_0 = 2.0023$, g error $\pm 1 \times 10^{-4}$). On lowering temperature from room temperature to 4 K, the Dysonian component in C_8K_{ex} spectrum coincides with temperature dependence of the EPR spectrum of C_8K sample (a stoichiometric one). The second component, the Lorentzian one at $g = 2.0045$, is due to localized electrons. This component follows Curie law on cooling. On lowering temperature, a very strong oscillations in EPR spectrum have been observed for C_8K_{ex} . These oscillations make difficult or even unable to analyze EPR (Fig. 3). The oscillations occur in different temperature regions in successive experiments. The highest temperature at which oscillations start was 160 K. However this temperature most frequently was close to 80 K (Fig 4). If the oscillations have large amplitude, they occur in the narrower

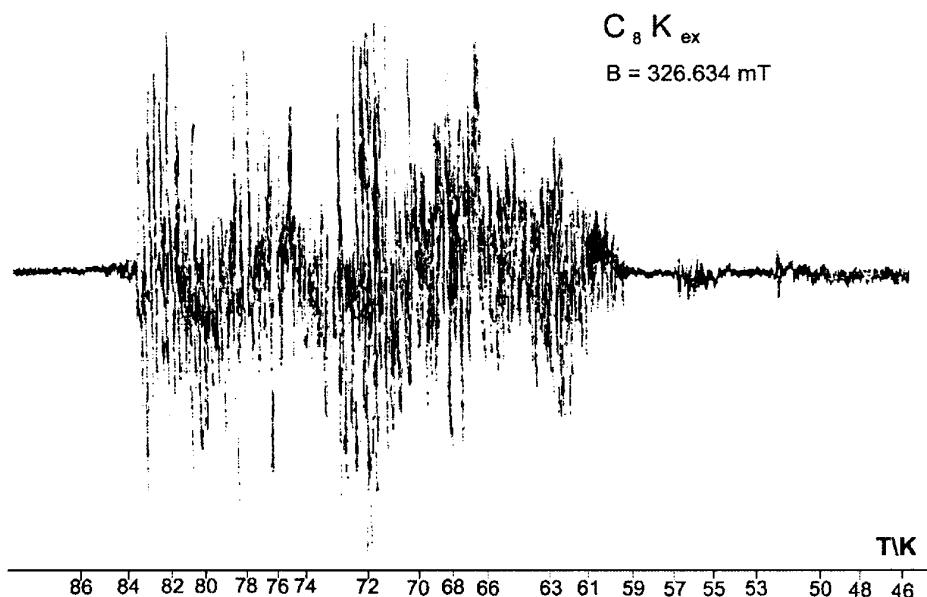


Fig. 4 Temperature evoked instabilities of C_8K_{ex} system as the strong oscillations registered at magnetic field close to EPR resonant value.

temperature range and EPR can-not be recorded at all. Less strong oscillations can persist down to 4 K. In that case EPR spectrum can be recorded and analyzed although there is significant noise due to oscillations. Generally, temperature at which the oscillations occur, their range and the amplitude of oscillations seem to occur at random. Such behavior can be related to local instability of stoichiometry in C_8K_{ex} sample. We propose that local concentration of C_6K (C_6Li -like structure) or even more dense K-graphite structures are possible in C_8K_{ex} sample. Thus, the coexistence of $2 \times 2 R0^\circ$ and $\sqrt{3} \times \sqrt{3} R30^\circ$ structures [14] of intercalated potassium in graphite can be present. These additional local concentrations can give Lorentzian line at 2.0045 in EPR of C_8K_{ex} . Our C_8K_{ex} sample contains small amount of oxygen as an impurity. Oxidized potassium leads to more dense K-graphite compounds [3]. Slight oxidation of C_8K_{ex} sample do not allow us to postulate local, unstable C_4KO_x - potassium double layer structure ($x < 0.2$). However, a very weak microwave absorption [7,15]

occasionally registered close to 4 K in C_8K_{ex} sample, suggests the presence of a very low content of superconducting phase or chaotic magnetic phase. Relatively high T_c means more dense K_xC with $x < 6$ [1].

To verify our assumptions the special K-graphite potassium double layer sample has been prepared. The nominal composition of the sample was C_6KO_y . The sample was a mixture of C_8K phase and C_4KO_x ($x < 0.2$) - potassium double layer phase [3]. For this sample EPR oscillations appeared also on lowering temperature. These oscillations differ from those observed for C_8K_{ex} system in one significant point: it was able to detect time dependent stabilization of two component structure. For example a period of 10 min was needed to restore smooth EPR at 100 K. This process is shown in Fig.5.

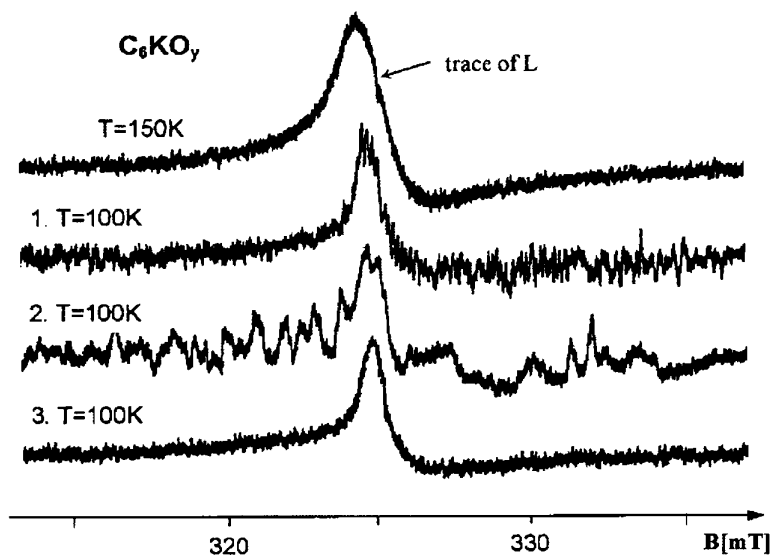


Fig. 5 EPR spectra of C_6KO_y with oscillations close to 100K. Smooth EPR was restored after 10 min at 100K. Steps 1., 2. and 3. are separated by periods of 5 min.

Mixed two phases C_4KO_x and C_8K can also easily redistribute potassium ions between stiffened graphitic planes on cooling. For both samples the phenomenon occurs accidentally in terms of temperature range because it is strongly related to thermal history of the sample: the rate of cooling the sample, the temperature and time of storage the sample between succeeding experiments.

Conclusions

For the first time the EPR oscillations of unstable graphitic structures are described. The EPR experiments were performed for a selected graphite and graphite-like structures: HOPG, C_8K , C_8K_{ex} , and C_6KO_y ($C_4KO_x + C_8K$). The EPR of pristine HOPG and stoichiometric C_8K coincide with reported previously while the EPR of C_8K_{ex} and C_6KO_y ($C_4KO_x + C_8K$) shows fluctuating, nonresonant oscillations on cooling the samples.

In case of C_8K_{ex} we propose that redistribution of the excess of potassium ions

between stiffened graphite planes creates local C_6K configuration. This local phase can originate from slightly shifted potassium ion inbetween graphite planes - it leads to the coexistence of $2 \times 2 R0^\circ$ and $\sqrt{3} \times \sqrt{3} R30^\circ$ structures. Such situation is realized at higher temperatures, where the unstable structure corresponds to coexistence of C_8K (dominating) and local C_6K or even more dense phase. Cooling the sample generates stiffening of the graphite planes, hence potassium ions are forced to be redistributed between the planes. Therefore, in C_8K_{ex} , the EPR oscillations reflect jump-like displacements of potassium between neighboring hexagons of graphite plane. The amplitude of the oscillations depends on the number of electrons transferred from conduction band of C_8K (Dysonian line characterized by two relaxation processes) to localized state C_6K (relatively narrow Lorentzian line characterized by one relaxation process). Such process should modulate conducting band - as the result conducting electrons give broad EPR spectrum with fluctuating g-values. In semiconducting systems, for example, broad spectrum of g-values can be observed due to different effective mass of carriers [16].

We postulate that C_6K phase (or a more dense one) exists even if there is no X-ray evidence - X-ray for the C_8K_{ex} shows only stoichiometric C_8K and metallic potassium. This implies that X-ray method is less sensitive than EPR to such process.

EPR of C_6KO_y ($C_4KO_x + C_8K$) sample shows also oscillations with time dependent stabilization. It strongly support our assumptions on temperature evoked redistribution of potassium ions inbetween graphite planes in described unstable systems.

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