

Skyrmion-Like Solitons, Topological Quasi-Positroniums, and Soliton-Catalytic Effects in Graphite-Potassium Intercalation Compounds and Metal Surfaces

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Abstract

We have analyzed the narrow components in the positron annihilation angular correlation spectra of graphite-potassium intercalation with the theoretical formula, which is extended from “topological quasi-positronium” model and discusses the relation to the catalytic activity of hydrogens. One mechanism of the soliton-catalytic effect is proposed.

Keywords

Model of Surface Chemical Reactions, Catalysis, Alkali Metal, Positron, Positron Annihilation

1. Introduction

It is known that alkali-metal graphite intercalation compounds (AGIC) have catalytic activities for hydrogen layer of the compounds. The behaviors of these compounds have been known to depend on the structure, sort of metals and temperature. Hydrogens are physisorptively accommodated in the molecules in the interstices among the alkali-metal ions in intercalant layers of stage-2 compounds $C_{24}M$ ($M = K, Rb$ and Cs) at temperatures below 200 K [1]-[3]. Chemisorption of hydrogen takes place in both first and second stage compounds at higher temperatures [4] [5]. In order to clarify the mechanism of hydrogen chemisorption in the graphite compounds and properties of hydrogen-absorbed graphite compounds, several studies have been carried out. The change in magnetic susceptibilities as a function of hydrogen content has been investigated for hydrogen-chemisorbed C_8K [6]. It has been suggested that dissolved hydrogen in C_8K is paramagnetic by means of magnetic resonance stu-

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dies [7]. The studies of means of ESR and electrical conductivity [8] have shown that in C_8K , $C_{24}K$, and $C_{24}Rb$, the hydride ions are stabilized after the dissociation of the hydrogen molecules into atoms and the subsequent charge transfer, and in C_8Rb hydrogens are absorbed in the atomic form.

Positron annihilation spectroscopy is a useful method in the study of electronic structures of materials. This spectroscopy has been used in the investigation of electronic structures in graphite and AGICs. The momentum distribution of σ and π -electrons in a graphite crystal has been studied by angular correlation of positron annihilation radiation (ACPAR) [9]-[12], and by Doppler-broadening positron-annihilation radiation (DBPAR) [13]-[15]. ACPAR spectra of C_8K and $C_{24}K$ after subtraction of a broad contribution account for annihilation with the graphite σ and π -electrons. Features of the narrow components in ACPAR spectra are in good agreement with the quasi-two dimensional electronic structures, which might correspond to the interlayer state with quasi-two dimensional free electron character parallel to the carbon planes [16]. In addition, hydrogen physisorption and chemisorption effects in AGICs have been studied by DBPAR [17]-[20]. The DBPAR spectra line shape of C_8K became sharp through hydrogen chemisorption at 300 K [17] [18], while the spectral line-shape of $C_{24}Cs$ became broad through the physisorption of hydrogen molecules at 77 K [18] [19]. The intensity of the narrow component of DBPAR spectrum of C_8Rb was suppressed through hydrogen absorption at 300 K, while it decreased at first and then increased through the absorption at the 373 K [20]. From the change in DBPAR spectral line-shape of C_8Rb , the hydrogen accommodated in C_8Rb is considered to be atomic at 300 K and to be in the form of the hydride ion at 373 K. Recently, the present authors have discussed the mechanism of anomalous magnetic effect due to hydrogen uptake in C_8RbH_x with the theoretical formula, which is extended from “topological quasi-hydrogen” model. It is suggested that the hydrogen state in C_8RbH_x might have the Kondo-like property. There exist some problems in the assumption that the narrow component of positron annihilation spectra corresponds to the interlayer state in AGICs. That is, the energy level of the interlayer state in the second-stage AGICs is above Fermi energy E_F . Furthermore, it looks like that the narrow component is not attributed to the simple positronium P_S in AGICs, because simple P_S cannot exist in the metallic state of AGICs.

In this study, we analyze the ACPAR spectra in $C_{24}K$ [21] with the theoretical formula, which is extended from “topological quasi-positronium” model [22] and discuss the origin of the anisotropic narrow components in ACPAR spectra, and relation to the catalytic activity of hydrogens in AGICs.

2. A Model System and the Soliton-Like Quantum Fluctuation

The structure of the stage-2 GIC $C_{24}K$ is shown in **Figure 1**. In the stage-2 GIC $C_{24}K$, the atomic density of potassium metal atoms intercalated between graphite layers is reduced to 2/3 of the density of the close-packed structure in the stage-1 compound, taking into account the difference in composition between the stage-1 compound C_8K and the stage-2 compound $C_{24}K$. According to the electronic structure model [16], there coexist quasi-two dimensional graphite π -bands, bands originating from potassium-metal s electrons, and the electronic

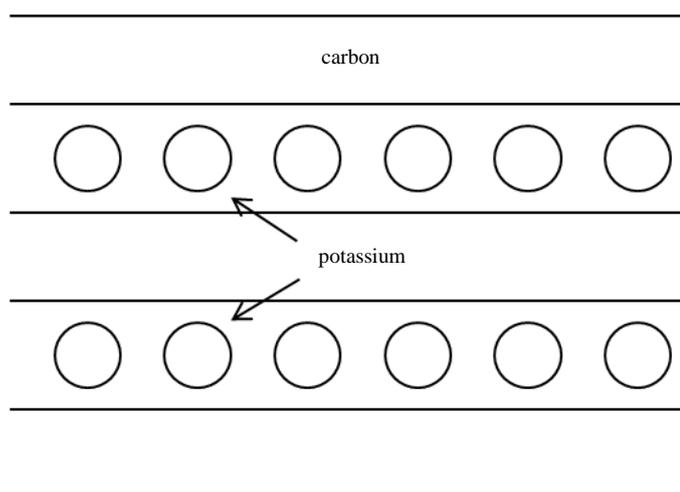


Figure 1. The structure of the stage-2 GIC $C_{24}K$. The carbon planes and potassium planes have overlapped by turns.

interlayer state in the stage-2 GIC $C_{24}K$, as shown in **Figure 2(a)**. The Fermi energy E_F and the location of the bands are determined by a balance between electronic and lattice energies. The electronic interlayer states were introduced by Posternak *et al.* [16]. These interlayer states, which exhibit free-electron character parallel to the layers, form a quasi-two dimensional band close to the Fermi energy.

Now, we shall consider the quantum fluctuation for investigation of quasi (2 + 1) electron state's system. In this study, we propose a kind of quasiparticle “the topological quasi-positronium”, based on the famous quantum fluctuation mechanism by Polyakov [23]. Polyakov [23] explained relatively strong quantum fluctuation in (2 + 1) system as follows. That is, the hedgehog solution [24] [25] in (3 + 1) system induces instanton-like quantum fluctuation in (2 + 1) system.

Now, we introduce the Lagrangian density,

$$L = \psi^\dagger \left(i\partial_0 - g_1 T^a A_0^a \right) \psi - \frac{1}{2m} \psi^\dagger \left(i\nabla - g_1 T^a A_{\mu(\neq 0)}^a \right)^2 \psi - \frac{1}{4} (F_{\mu\nu})^2 + \frac{1}{2} \left(\partial_\mu \Phi_a - g_2 \varepsilon_{abc} A_\mu^a \Phi_c \right)^2 - \lambda^2 \left(\Phi_a \Phi_a - \eta^2 \right)^2 \quad (1)$$

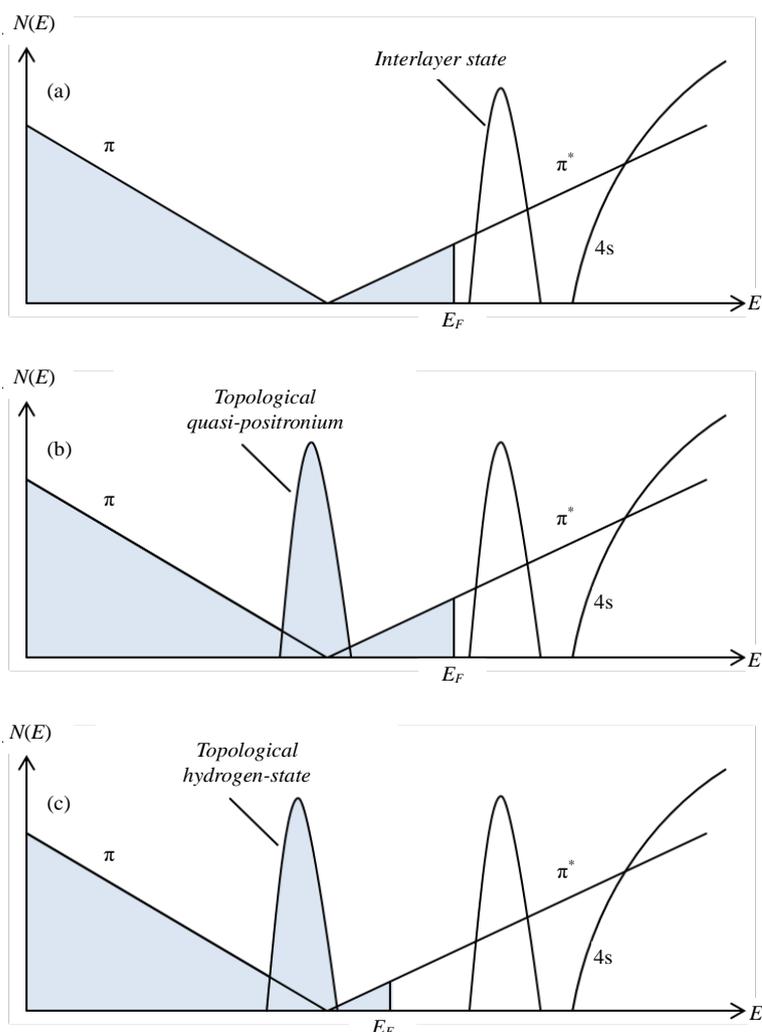


Figure 2. (a), (b), (c) The electronic structure model of (a) alkali-metal GICs and we consider that (b) “topological-quasi-positronium” exists from the result of ACPAR, and (c) absorbed hydrogen alkali-metal GICs. $4s$ denotes the alkali-metal s band. π and π^* denote graphitic bands. The electronic structure changes by absorbing hydrogen.

where ψ is the positron field and Φ is the scalar field. The first and second terms in Equation (1) shows the kinetic energy of positron field and the interaction between the positron field and gauge field. The third term corresponds to the kinetic energy of the gauge field. The fourth term shows the kinetic energy of the scalar field and the interaction between the scalar field and gauge field. The fifth term shows the effective potential.

Here, we set the symmetry breaking $\langle 0|\Phi_a|0\rangle=(0,0,\eta)\equiv\phi_n$ of the charged scalar field Φ_a . We change the field Φ_a with a zero asymptotics at infinity.

$$\Phi_a \rightarrow \phi_n + \phi_a \tag{2}$$

Then we enter Equation (2) into Equation (1) and can introduce the effective Lagrangian density as follows.

$$\begin{aligned} L_{\text{eff}} = & \psi^+ (i\partial_0 - g_1 T^a A_0^a) \psi - \frac{1}{2m} \psi^+ (i\nabla - g_1 T^a A_{\mu(\neq 0)}^a)^2 \psi - \frac{1}{4} (F_{\mu\nu})^2 \\ & + \frac{1}{2} (\partial_\mu \phi_a - g_2 \varepsilon_{abc} A_\mu^b \phi_c)^2 + \frac{m_1^2}{2} \left[(A_\mu^1)^2 + (A_\mu^2)^2 \right] + m_1 \left[A_\mu^1 \partial_\mu \phi_2 - A_\mu^2 \partial_\mu \phi_1 \right] \\ & + g_2 m_1 \left[\phi_3 \left[(A_\mu^1)^2 + (A_\mu^2)^2 \right] - A_\mu^3 \left[\phi_1 A_\mu^1 + \phi_2 A_\mu^2 \right] \right] - \frac{m_2^2}{2} (\phi_3)^2 - \frac{m_2^2 g_2}{2m_1} \phi_3 (\phi_a)^2 - \frac{m_2^2 g_2^2}{8m_1^2} (\phi_a \phi_a)^2 \end{aligned} \tag{3}$$

where, $m_1 = \eta g_2$, and $m_2 = 2\sqrt{2}\lambda\eta$.

Here, it is convenient to choose the following gauge condition.

$$\phi_1 = 0, \phi_2 = 0, \partial_\mu A_\mu^3 = 0 \tag{4}$$

When the determinant of the infinitesimal transformation operator in this gauge condition is expressed by $\det M$, the generating function of Green function is

$$Z(J, \eta, \bar{k}, k) \sim \int \exp \left\{ i \int (L_{\text{eff}} + J \cdot A + \eta \cdot \phi + \bar{k} \cdot \psi + \bar{\psi} \cdot k) d^3x \right\} \prod_x \det M dA d\phi d\psi d\bar{\psi} \tag{5}$$

where J, η, \bar{k} and k are the sources of the field A_μ, ϕ_a, ψ , and $\bar{\psi}$. Taking into account that ϕ_n is a kind of the vacuum state ϕ_3 corresponds to the soliton-like-field introduced by t’Hooft [26], based on the disorder parameter [27] [28]. A charged skyrmion-like soliton in quasi (2 + 1) intercalate state in AGICs might be described as a topological soliton [22] [29] [30]-[32] “Topological quasi-positronium” is regarded as the skyrmion-like soliton, which traps a positron, of the electron-density. “Topological quasi-hydrogen” is regarded as the skyrmion-like soliton, which traps a proton, of the electron-density. Fermion number densities $J_{\text{sky}}^P(r)$ and $J_{\text{sky}}^H(r)$ of “topological quasi-positronium” and “topological quasi-hydrogen” are represented, respectively, in the case of the SU(2) pseudospin-like skyrmion configuration [30]-[32].

$$J_{\text{sky}}^P(r) = |\phi_3|^2 = \frac{1}{\pi} \frac{4\xi_p^2}{[r^2 + 4\xi_p^2]^2}.$$

$$J_{\text{sky}}^H(r) = |\phi_3|^2 = \frac{1}{\pi} \frac{4\xi_H^2}{[r^2 + 4\xi_H^2]^2}.$$

$$\xi_H \sim \frac{1}{2} \xi_p.$$

Then $J_{\text{sky}}^P = |\phi_3|^2$ is to be thought to be the induced soliton-like electron density in quasi (2 + 1) system. Really the quasi(2 + 1) system is derived from the instanton-like fluctuation of these solitons [33]. **Figure 3(a)** shows the positron annihilation spectrum for pair-momentum p perpendicular to the crystallographic c -axis ($P \perp c$) in C₂₄K [21]. Assuming p -distribution of the narrow component ($p \perp c$) of the positron annihilation spectrum is isotropic, p -distribution of the narrow component ($p \perp c$) is shown in **Figure 3(b)**. **Figure 3(c)** shows the auto-correlation function of the electron-wave function perpendicular to the c -axis, which is fourier-transformed from the narrow component for pair-momentum p perpendicular to the c -axis. The solid line in **Figure 3(c)** shows the function $J_{\text{sky}}^P(r)$. The value of ξ_p is estimated to be $\sim 2.1 \text{ \AA}$. The dotted line in **Figure 3(c)** shows the function $J_{\text{sky}}^P(r)$ with $\xi_H \sim 1.0 \text{ \AA}$, approximately.

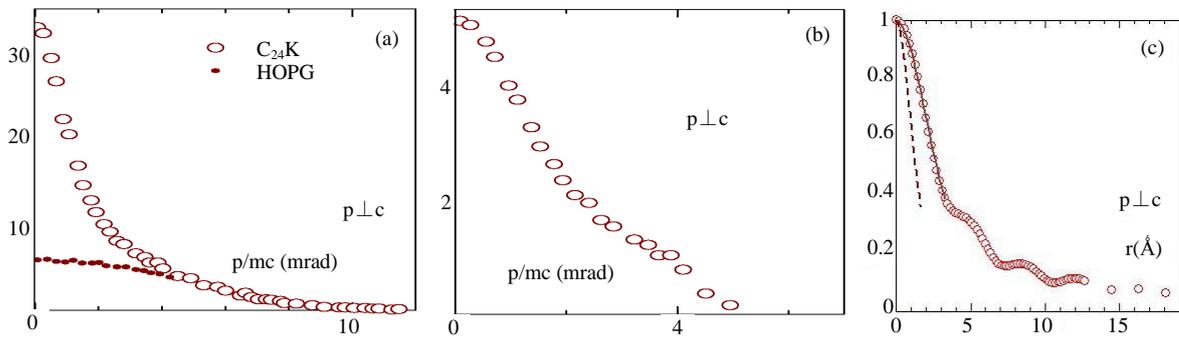


Figure 3. (a) The positron annihilation spectrum for pair-momentum p perpendicular to the c -axis in $C_{24}K$ [21]. (b) p -distribution of the narrow component perpendicular to the c -axis. (c) The autocorrelation function of the electron-wavefunction perpendicular to the c -axis. The solid line in Figure 3(c) shows the function $J_{sky}^P(r)$ with $\xi_P \sim 2.1 \text{ \AA}$. The dotted line in Figure 3(c) shows the function $J_{sky}^P(r)$ with $\xi_H \sim 1.0 \text{ \AA}$.

Here we shall introduce one mechanism of the soliton-catalytic effect as follows. The effective lagrangian for non-abelian gauge fields A_μ in the presence of a soliton ϕ_3 is

$$L_{eff} = \frac{1}{16\pi} \int d^3x \frac{\phi_3(x_3)}{|\phi_3(x_3)|} \varepsilon^{\mu\nu\alpha} \text{tr} \left(A_\mu \partial_\nu A_\alpha + \frac{2}{3} A_\mu A_\nu A_\alpha \right)$$

where the x_3 is parallel to c -axis and the plane (x_1, x_2) is perpendicular to c -axis. The corresponding variation of L_{eff} under an infinitesimal gauge transformation is

$$\begin{aligned} \delta_\omega L_{eff} &= \frac{1}{16\pi} \int d^3x \frac{\phi_3(x_3)}{|\phi_3(x_3)|} \varepsilon^{\mu\nu\alpha} \partial_\mu \text{tr} (\omega \partial_\nu A_\alpha) \\ &\sim -\frac{1}{4\pi} \int d^3x \varepsilon^{ab} \text{tr} (F_{ab} \omega) \end{aligned}$$

This shows parity anomaly. That is, the soliton-like electron density in the interlayer state induces parity anomaly quantizely. It is suggested that the soliton-like electron density in the interlayer state might induce the parity change, from the bonding electron wave function to the anti-bonding one, in the hydrogen-molecule in the interlayer in AGICs to cancel the parity anomaly.

3. Conclusion

We have analyzed the narrow component in the positron annihilation angular correlation spectra in the second stage graphite-potassium intercalation $C_{24}K$ with the theoretical formula extended from “the topological quasi-positronium” model and have discussed the relation to the catalytic activity of hydrogens in AGICs.

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