Quasi-Two Dimensional Metallic Hydride State and the Soliton-Catalytic Effect in Alkali Metal Hydrogen-Graphite Intercalation Compounds

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We have discussed the mechanism of anomalous magnetic effect due to hydrogen uptake in C₈RbHₓ with the theoretical formula, which is extended from “topological quasi-hydrogen” model. It is suggested that the hydrogen-state in C₈RbHₓ might have the Kondo-like property. [DOI: 10.1380/ejssnt.2012.226]

Keywords: Models of surface chemical reactions; Chemisorption; Catalysis; Positron; Hydrogen

I. INTRODUCTION

The charge transfer complexes between graphite and alkali metals are called “alkali-metal-graphite intercalation compounds (AGICs)” where graphite is an extreme of the polycyclic condensed aromatic hydrocarbons, consisting of an infinite network of benzene rings. AGICs are very interesting materials, which have quasi-two-dimensional electron structures [1]. In these AGICs, alkali-metal atoms are intercalated in the galleries between graphite sheets. The compound with alkali-metal atoms in every gallery is called a stage-1 GIC, while ones with alkali-metal atoms in every n gallery are named stage-n GICs. The approximate compounds of stage-1 and stage-n AGICs are described as C₈M and C₁₂ₓM, where M=K, Rb, and Cs. It has been known that AGICs have catalytic activity for hydrogen and absorb hydrogen chemisorptively to form alkali metal hydride GICs through the dissociation of hydrogen molecules and charge transfer from AGICs to hydrogen [2, 3]. The stage-1 graphite-potassium compound CₛK, with a golden loster, is known to fix hydrogen and to become a dark blue compound CₛKH₂/₃, which have the second stage structure [3, 4]. The behaviors of hydrogen absorption and catalytic activities of AGICs have been known to depend on the structure, sort of metals and temperature. The hydrogen chemisorption mechanism in AIGCs is not clear at the present time.

Cartier et al. [5, 6] have reported very interesting and important results of angular correlation of positron annihilation radiation (ACPAR) for AGIC. That is, it is seen that a strong anisotropic and narrow component appears in the center of ACPAR, of CₛK, Cₛ₂K, and CₛRb, after subtraction of a broad contribution which accounts for annihilation with the graphite π- and σ-electrons [7–10]. Features of the narrow component in the ACPARs are in good agreement with quasi-two dimensional band structure, which might correspond to the interlayer state with quasi-two dimensional free-electron character parallel to the carbon planes [11]. Then hydrogen chemisorption and physisorption effects in AGICs have been studied by means of positron annihilation [12–15].

Enoki et al. [3] found out an interesting magnetic effect due to hydrogen uptake in C₈RbHₓ. That is, in the ESR measurement, C₈Rb gives an asymmetric signal for the conduction electron spin resonance due to the Pauli paramagnetism of the conduction electrons. The introduction of hydrogen generates a new broad asymmetric signal, superposed on the signal of the conduction electron spin resonance. The temperature dependence of the newly generated signal obeys the Curie-Weiss law, suggesting the presence of localized spins. The observed magnitude of the asymmetry parameter of the signal, θ/θ = 1.8–3.0, suggests that the localized spins exist in the metallic medium of C₈RbHₓ. This magnetic effect due to hydrogen has not been observed in C₈KH₂ [5–7].

In this study, we discuss the mechanism of the anomalous magnetic effect due to hydrogen uptake in C₈RbHₓ with the theoretical formula, which is extended from “topological quasi-hydrogen” model [16].

II. A MODEL SYSTEM AND THE KONDO-LIKE EFFECT

Enoki et al. [17] have explained that the activation process, where the alkali metal atoms are displaced, will exist in the transition from a state with atoms H⁻ to a state with anions H⁻, as illustrated in Fig. 1. The energy change due to the transition from the neutral state (C₈M⁺H⁻) to the ionic one (C₈M⁺ + H⁻) is estimated to be IP-EA-Δ, where IP is the ionization potential of C₈M,
the electron affinity of hydrogen, and $\Delta$ the Madelung energy change. Meanwhile, when alkali metal atoms react with graphite to form the intercalation, the distance between alkali metal atoms is elongated from the distance in the pure metals. The atom-atom distances are 4.05 and 4.32 Å in pure K and Rb metals, respectively.

In stage-1 AGICs, the atom-atom distance is 4.92 Å for both K and Rb. The amounts of the increase of the distance in the compounds are 21 and 14% of the distance in the pure metals K and Rb, respectively. The elongation of the distance depresses the interactions among the alkali metal atoms. Alexander et al. [20] have shown that the Debye temperatures of CsK and CsRb are 374 K and 439 K, respectively. Thus, while the Rb triangular lattice in the graph of the graphite layers is comparably rigid, the interaction among K atoms is weakened so much that it is easy to displace the positions of K atom in the compound. So the activation energy is considered to be smaller for CsK than for CsRb as shown in Fig. 1. The activation energy for CsK is comparable with the thermal energy $k_B T$ at room temperature. On the other hand, for CsRb, the activation energy is so large that the neutral state with the dissociated hydrogen atoms is stabilized. This is consistent with the experimented result by positron annihilation method [15]. In stage-1 CsRb, because of the large screening effect, it looks like that stable simple-neutral hydrogen state might not exist in the metallic interlayer state of CsRb.

One (I.K.) of the present authors has suggested strongly the electronic stage of “topological quasi-postitronium”, which is composed of the positron and the induced soliton-like electron density around the positron in the interlayer state in AGICs. Taking into account “topological quasi-postitronium” model in the interlayer state in AGICs, “topological quasi-hydrogen”, which is the proton and the induced soliton-like electron density (fermion number density $\rho_{top}(r)$) around the proton in the interlayer state, might be created in the interlayers in CsRbH$_x$.

The Anderson Hamiltonian, $H_{AN}$, with a single soliton-like orbitals of “topological quasi-hydrogen” is

$$H_{AN} = \sum_{k,\sigma} \varepsilon_k C^+_{k\sigma} C_{k\sigma} + \sum_{k,\sigma} V_k \left( C^+_{k\sigma} a_{\sigma} + a_{\sigma}^+ C_{k\sigma} \right)$$

$+ \varepsilon_{top} \sum_{\sigma} a_{\sigma}^+ a_{\sigma} + U a_{\uparrow}^+ a_{\uparrow} a_{\downarrow}^+ a_{\downarrow}$.

where $\varepsilon_k$ is the energy of quasi-two dimensional electron in the interlayer state in CsRbH$_x$. $\varepsilon_{top}$ is the unperturbed energy of the electron-wavefunction, $\psi_{top}$ on “topological quasi-hydrogen”.

Here $\varepsilon_k$ is the energy of the unperturbed electron for the electron of the Wavefunction $\psi_{top}$ and spin state $\sigma$, respectively. Supposing that $V_k$ does not depend on $k$ and values of $|\varepsilon_{top}|$ and $V$ are small compared with the Fermi energy. $H_{AN}$ is simplified as follows.

$$H_{AN} = \sum_{k,\sigma} \varepsilon_k C^+_{k\sigma} C_{k\sigma} - J \sum_{k,k'} S^z \left( C^+_{k\uparrow} C^+_{k'\uparrow} - C^+_{k\downarrow} C^+_{k'\downarrow} \right) + S^+ C^+_{k\downarrow} C_k^+ + S^- C^+_{k\uparrow} C_k^- + 2\mu_B HS_z. \quad (2)$$

$S$ is the spin operator for “topological quasi-hydrogen” which is assumed to have the magnitude 1/2 for simplicity, and $S_{\pm} = S_{\uparrow} \pm i S_{\downarrow}$.

$$J = V^2 \left( \frac{1}{\varepsilon_{top}} - \frac{1}{\varepsilon_{top} + U} \right).$$

Fermion number density $\rho_{top}(r)$ of “topological quasi-hydrogen” is represented approximately in the case of spherically symmetric charge 1 Skyrmion-like soliton [24] as follows,

$$\rho_{top}(r) \equiv \psi_{\text{top}}^+(r) \psi_{\text{top}}(r) = |\psi_{\text{top}}(r)|^2$$

$$\propto f'(r) \frac{\sin^2 f(r)}{r^2},$$

where the profile function $f(r)$ is given from the standpoint of the Skyrmion-like soliton, which is introduced from instantons [25] as follows,

$$f(r) = \pi \left[ 1 - \left(1 + \frac{\lambda^2}{r^2} \right)^{-1/2} \right],$$

where $\lambda$ is the radius of the soliton.

$\chi = \left( \frac{\mu_B^2}{\beta} \right) \left( [\beta - 2(u_1 - u_2...)]^2 \right), \quad (4)$

FIG. 2: Open and shaded circles between the carbon layer represent H$^-$ ion and K$^+$ ion, respectively.
where \( \beta \) is \( 1/k_B T \) and

\[
S' = -(2 - \varepsilon) \sum_{i>j} (-1)^{i-j+1} \left[ \log \sin \left( \frac{\pi (u_j - u_i)}{\beta} \right) - \log \sin \left( \frac{\pi}{\beta \varepsilon F} \right) \right].
\]

\( u_i \) is the position of an instanton or anti-instanton.

\[
\varepsilon = \left( \frac{8 \delta_0}{\pi} \right) \left( 1 - \frac{\delta_0}{\pi} \right)
\]

\[
\tan \delta_0 = - \frac{\pi J \rho}{2}
\]

\( \rho \) is the density of the electron states. In high temperature condition \( (T > J/k_B T) \),

\[
\langle [\beta - 2(u_1 - u_2 - \ldots)]^2 \rangle \propto \beta^2
\]

Thus

\[
\chi = \left( \frac{\mu_B^2}{\beta} \right) \beta^2 \sim \mu_B^2 \beta \sim \frac{\mu_B^2}{T}.
\]

This indicates that the susceptibility \( \chi \) is in Curie-Weiss law, and is consistent with the ESR experiment [17], which suggests that the localized spins exist in the metallic medium of \( \text{CsRbH}_x \). In the case of \( \text{CsKH}_x \), the intercalates in the \( \text{CsKH}_x \) at \( x = 0.67 \sim 0.8 \) form \( K^+ - H^- \) triple atomic layers along the graphite sheet stacking [22, 23], which is a favorable arrangement for gaining ionic lattice energy, as shown in Fig. 2. \( H^- \) ions in \( \text{CsKH}_x \) do not have the localized spin.

### III. CONCLUSION

We have discussed the mechanism of the anomalous magnetic effect due to hydrogen uptake in \( \text{CsRbH}_x \), which indicates the localized spins in the medium of \( \text{CsRbH}_x \). It is suggested that the hydrogen-state in \( \text{CsRbH}_x \) might have the Kondo-like property.

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