Two-Dimensional Metallic Hydrogen in the Potassium-Hydrogen-Graphite Ternary Intercalation Compound

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A proton NMR study was carried out in the stage-1 potassium-hydrogen-graphite ternary intercalation compound C_4KH_x, prepared through direct intercalation of potassium hydride into graphite. Line-shape analysis revealed extremely dense two-dimensional packing of negatively charged hydride ions where hydrogen-hydrogen direct contact takes place. The metallic nature of hydrogen was observed through the Korringa term, $(T_1T)^{-1}=6.4\times10^{-4}$ s^{-1}K^{-1}, where T_1 is the spin-lattice relaxation time. C_4KH_x is thus proved to be an example of two-dimensional metallic hydrogen.

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Among metal-hydrogen systems there are two extreme cases: transition-metal hydrides and alkali-metal hydrides. Transition-metal hydrides such as PdH_x are considered to be metal-hydrogen alloys with a delocalized electronic nature of the hydrogen, associated with the strong mixing of the hydrogen 1*s* state and the transition-metal electronic states. On the other hand, alkali-metal hydrides such as KH are ionic insulators and can be described in terms of hydride anions H^- with localized electronic states. Recently, the potassium-hydrogen-graphite ternary intercalation compounds (KH-GIC's) $C_{4n}KH_x$ (*n* is the stage number) have attracted attention as a new class of metal-hydrogen system between the two extremes. In $C_{4n}KH_x$, the experimental results of x-ray diffraction,[1] specific heat,[2] Shubnikov–de Haas oscillation,[3] and optical reflectance spectra[4] were consistent with the picture of ionic layers stacking in the sequence K^+-H^--K^+ between the host graphite planes. The relatively strong electron affinity of hydrogen causes charge transfer from graphite and potassium to hydrogen, and it reduces the total electronic density of states at the Fermi level compared with C_8K. It was therefore believed that the principal atom-atom interaction in the intercalate was the K^+-H^- ionic attraction, and the intercalated hydrogen (hydride ion) had a localized electronic character. However, recent experiments on thermoelectric power[5] and proton NMR[6-8] revealed that the anionic hydrogen has a weakly metallic nature. This fact showed that the amount of charge transfer to hydrogen is not enough to form purely monovalent anions (H^-), so that a hole band originating from the hydrogen 1*s* state is located across the Fermi level.

KH-GIC's are synthesized through two different paths. One is the chemisorption of hydrogen gas into stage-1 C_8K.[9,10] Hydrogen uptake brings about a stage change, and the reaction product is stage-2 C_8KH_x with a saturated hydrogen concentration of $x=0.67$. Guérard *et al.*[1] reported a new synthesis method with a direct intercalation of potassium hydride into graphite. Either stage-1 or stage-2 compounds were prepared depending on the heat-treatment temperature and a higher hydrogen concentration ($x=0.8$) was achieved through this method. The latter method is attractive because the stronger hydrogen-hydrogen interaction expected in a compound having higher hydrogen concentration is a desirable aspect in enhancing the metallic character of hydrogen. While the NMR studies to date have been confined to the stage-2 compounds made from chemisorption of gaseous hydrogen, the present proton NMR experiment was done on the stage-1 C_4KH_x made through the direct-intercalation method, with particular emphasis on the relationship between the structure and the electronic state of hydrogen.

$(6\times12\times0.1)$-mm^3 slices of highly oriented pyrolytic graphite (HOPG) (Union Carbide Co.) were heat treated with potassium hydride at 430 °C for three weeks following the procedure of Guérard *et al.*[1] The obtained slices of C_4KH_x with well-defined *c* axes were electrically insulated by polytetrafluorethylene (PTFE) films and sealed in a Pyrex tube with 90 Torr of hydrogen and 30 Torr of helium gases. Fourier-transform proton NMR experiments were performed at 29.8 MHz in the temperature range 4.2–298 K.

The shape of the proton absorption line exhibited no distinct change between 4.2 and 298 K, showing that thermally activated motional narrowing is absent. The absence of hydrogen motion even at room temperature proves the existence of a strong ionic interaction between negatively charged hydride ions and potassium cations. The line shape was dependent on the orientation of the crystalline c axis relative to the external magnetic field (Fig. 1). The angular dependence of the second moment $\langle \Delta\nu^2 \rangle$ is shown in Fig. 2. $\langle \Delta\nu^2 \rangle$ takes its maximum value at 90°, and its minimum around 40°. The theoretical prediction for the line shape for the two-dimensional hydrogen lattice is given by the equations[7]

$$\langle \Delta\nu^2 \rangle = A f(\theta_0) \sum_h \sum_k r_{hk}^{-6}\,, \tag{1}$$

$$A = (1/4\pi^2) 3\gamma_n^4 \hbar^2 I(I+1)\,, \tag{2}$$

$$f(\theta_0) = \tfrac{1}{32}(27\cos^4\theta_0 - 30\cos^2\theta_0 + 11)\,, \tag{3}$$

where θ_0 is the angle between the c axis and the external magnetic field, r_{hk} is the internuclear distance, and $\sum_h \sum_k$ represents the lattice sum. Equation (3) predicts that the linewidth depends on θ_0, and takes a minimum value at $\theta_0 = 42°$. Figure 2 shows that the experimental angular dependence of $\langle \Delta\nu^2 \rangle$ is well explained by Eq. (3). This agreement reveals the planarity of the hydrogen lattice, although a small disagreement may be attributable to wrinkling of the layer. Another important feature of the line shape is that the observed $\langle \Delta\nu^2 \rangle$ is far larger than the value calculated by assuming the 2×2 hexagonal closest packing of hydride ions which is completed at a hydrogen concentration $x=0.5$. For example, at $\theta_0 = 0°$, the observed $\langle \Delta\nu^2 \rangle$ was 21.5 kHz^2 whereas 3.64 kHz^2 is calculated for the 2×2 hcp superlattice with respect to the host graphite. It is known that potassium ions are arranged in the two-dimensional 2×2 hcp structure in C_8K. Taking into account that the ionic radius[11] of an H^- ion (1.54 Å) is bigger than that of a K^+ ion (1.33 Å), the experimentally verified two dimensionality of the hydride lattice and the large linewidth demonstrate that the hydride ions must be extremely densely packed within a plane in this compound. Although the hydrogen positions have not been determined exactly, it is clear from the NMR absorption line that hydride ions are arranged in an extremely dense fashion in a plane, so that the hydrogen 1s orbitals overlap one another.

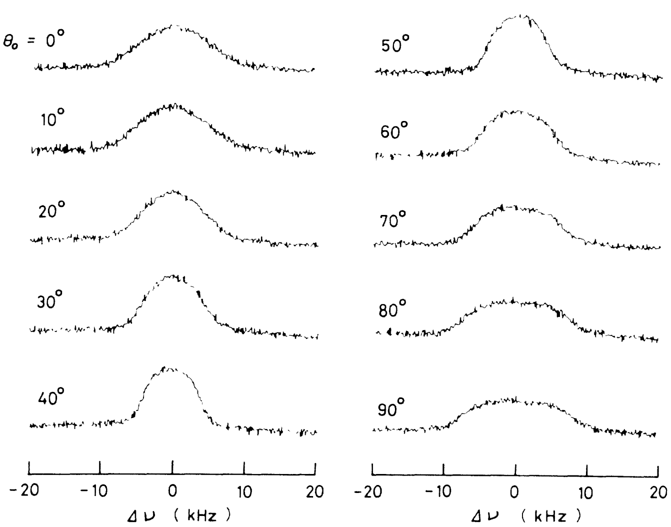

FIG. 1. Angular dependence of the proton NMR line at 77 K. θ_0 is the angle between the c axis and the external magnetic field.

To be more quantitative, a specific structural model was assumed. We note here that an in-plane unit cell, $2\sqrt{3}\times5R(0°,30°)$ rectangular superlattice, was reported by Guérard *et al.*[1] from the x-ray experiment. The NMR line shape was calculated by assuming this $2\sqrt{3}\times5$ superlattice, and putting hydrogen at appropriate positions. The results are shown in Fig. 2 for several different hydrogen concentrations. A comparison between the experimental data and the model calculations gives an estimation of the hydrogen concentration at $x=0.7$. Although this value is a littler smaller than the previous report ($x=0.8$) by Guérard *et al.*,[1] it is confirmed that the hydrogen concentration exceeds the saturation limit ($x=0.67$) attainable through the chemisorption method. It is noteworthy that the in-plane nearest H-H distance is revealed to be a very small value, 2.96 Å, at this concentration. This distance is smaller than the ionic diameter of an H^- ion, so that we can expect direct interactions between hydrogen atoms. (Note also that the nearest H-H distance in pristine po-

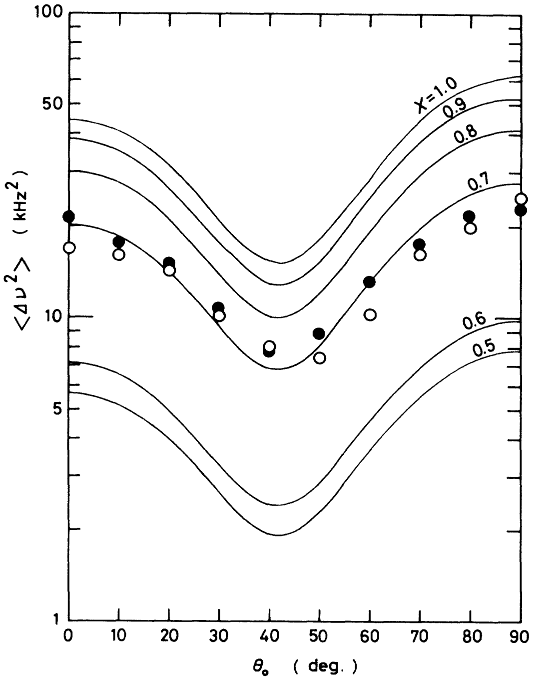

FIG. 2. Angular dependence of the second moments of the proton NMR lines in C_4KH_x. The data, ● and ○, were taken at 77 and 298 K, respectively. The solid lines were calculated from the $2\sqrt{3}\times5R(0°,30°)$ in-plane superlattice model as a function of hydrogen concentration x.

tassium hydride is 4.04 Å.) The structure model is illustrated in Fig. 3.

Direct observation of the metallic nature of hydrogen was obtained from the relaxation measurement. The experimental spin-lattice relaxation rates are depicted in Fig. 4, and the index for the temperature dependence of T_1^{-1} is proved to be unity, which means that the hydrogen is metallic. The Korringa product, $(T_1T)^{-1}$, is 6.4×10^{-4} $\mathrm{s}^{-1}\mathrm{K}^{-1}$. The local density of states at a hydrogen site is estimated to be $N_{\mathrm{H}}(E_F)=0.021$ state eV^{-1} per spin per atom of hydrogen. Compared with the total density of states obtained from the low-temperature specific-heat measurements,[2] the contribution of the hydrogen 1*s*-like hold band generates $\frac{1}{100}$ of the total metallicity in this compound.

The above analysis proves that a two-dimensional metallic hydrogen layer exists in C_4KH_x. The origins for this interesting electronic property are (1) the overlap of 1*s* orbitals due to extremely dense packing of hydride ions within a plane and (2) the incomplete charge transfer from potassium and graphite to hydrogen. When a large concentration of H^- ions are introduced in the intercalate space, the dispersive nature of the hydrogen 1*s* band is brought about due to direct H^--H^- interactions. This picture is also supported by the recent ultraviolet photoemission experiment on stage-2 C_8KH_x,[12] where a hydrogen-induced band was shown to exist near the Fermi level. Very recently a band-structure calculation by Mizuno and Nakao showed the existence of a metallic hydrogen band for stage-2 C_8KH_x,[13,14] and stage-1 C_4KH_x.[15] The band, which has the nature of the hydrogen 1*s* state, was found to intersect the Fermi level, and it was also shown that this band is almost dispersionless along the q_z axis while dispersive along q_x and q_y. Thus, the two kinds of two-dimensional Fermi surfaces, originating from an electron band of graphite π^* and a hole band of hydrogen 1*s*, were shown to coexist in the Brillouin zone of $C_{4n}KH_x$ ($n=1,2$). This result is quite consistent with our NMR result.

Recently, Saito *et al.*[8] reported an NMR study on stage-2 C_8KH_x ($x=0.61$) made from chemisorption of hydrogen gas into HOPG-based C_8K. Compared with their result, the proton NMR linewidth is about 30% larger in the present stage-1 compound, reflecting the stronger hydrogen-hydrogen interaction. The values of $(T_1T)^{-1}$ were, however, quite similar for the stage-1 and stage-2 compounds in spite of our expectation that the larger hydrogen concentration as well as the lower stage number might give rise to an increase in the electronic density of states at the Fermi level.

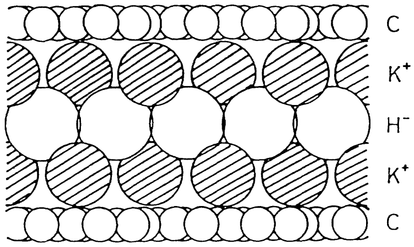

FIG. 3. The structural model of C_4KH_x with the $2\sqrt{3}\times5R(0°,30°)$ in-plane superlattice. The distance between the graphite layers is 8.54 Å.

In summary, we have shown that two-dimensional metallic hydrogen is realized by stabilizing an extremely densely packed hydride planar lattice with the incomplete charge-transfer state of $H^{-\delta}$ ($\delta<1$) in the galleries of graphite. In transition-metal hydrides, the strong mixing between the hydrogen 1*s* state and the metal electronic states makes the system far different from the concept of metallic hydrogen consisting of hydrogen 1*s* orbitals. In considering the conditions of realizing metallic hydrogen in the compound, the essential point is the presence of the hydrogen-hydrogen direct interaction. From this point of view, all of the alkali-metal hydrides are ruled out as candidates for metallic hydrogen except LiH. In LiH, which has an NaCl structure, direct interactions among neighboring hydrogen atoms are realized (the shortest H-H distance is 2.88 Å) because of the small size of the cation; however, the compound is not metallic due to perfect charge separation. Thus, the hydride metal in KH-GIC's is a unique finding and is expected to be a new target for searching for novel solid-state properties, including the possibility of high-temperature superconductivity based on metallic hydrogen.[16,17]

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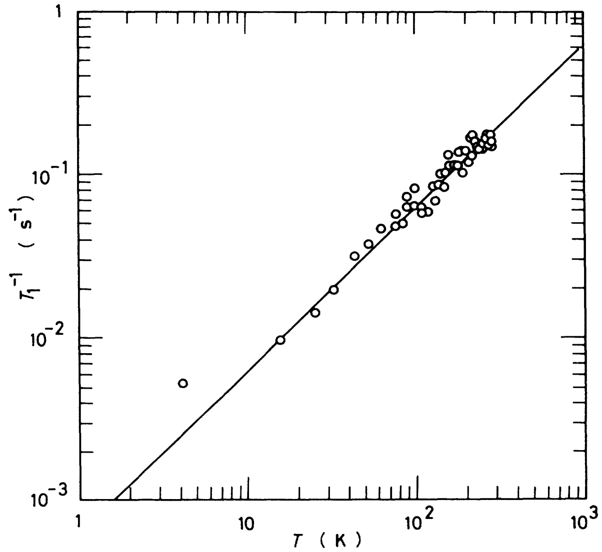

FIG. 4. Temperature dependence of the proton spin-lattice relaxation rates in C_4KH_x measured at 29.8 MHz and $\theta_0=0°$. The solid line represents the metallic relaxation mechanism, $(T_1T)^{-1}=6.4\times10^{-4}\,\mathrm{s}^{-1}\mathrm{K}^{-1}$.

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