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Charge Kondo Effect induced by valence skipping dopants in $Pb_{1-x}Tl_xTe$ and $Pb_{1-x}Na_xTe$ probed by ^{125}Te-NMR

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We have performed schematic ^{125}Te-NMR measurements in $Pb_{1-x}Tl_xTe$ (x = 0, 0.35, 1.0%) and $Pb_{1-x}Na_xTe$ (x = 0.46, 1.45%). Superconductivity occurs above $x \sim 0.3\%$ in $Pb_{1-x}Tl_xTe$ and superconducting temperature T_c reaches about 1 K at x = 1.0%. In $Pb_{0.99}Tl_{0.01}Te$, the ^{125}Te nuclear spin relaxation rate ($1/T_1T$) for Te sites near Tl dopants is unexpectedly enhanced in the normal state below a characteristic temperature of $\sim$ 10 K, below which the resistivity experiences an upturn. In contrast, no enhancement of $1/T_1T$ is observed at low temperatures for Te sites both near and far from non-valence-skipping Na dopants in $Pb_{1-x}Na_xTe$ with x = 1.45%. These results suggest the existence of valence fluctuations associated with the charge Kondo effect arising from Tl dopants in the superconducting sample $Pb_{1-x}Tl_xTe$ with x = 1.0%.

KEYWORDS: Charge Kondo effect, Superconductivity, NMR

1. Introduction

PbTe is a narrow-gap semiconductor. Small amounts of substitution of Tl for Pb (i.e., $Pb_{1-x}Tl_xTe$) lead to a superconducting (SC) ground state when x exceeds $x_c \sim 0.3\%$ [1–4]. Thallium is the only dopant known to cause superconductivity in PbTe, suggesting that these specific impurities have a unique effect on the electronic states near the Fermi energy. The SC transition temperature (T_c) reaches 1.5 K for $x_c \sim 1.5\%$ (the solubility limit) in spite of its low carrier density derived from a narrow-gap semiconductor, higher than that of other well-known low-carrier-density superconductors, such as $SrTiO_3$ [5]. The hole density obtained from the Hall coefficient measurement increases linearly with x up to x_c, indicating that Tl dopants behaves as an acceptor (Tl^{1+}). However, the increase of the hole density is gradually suppressed above x_c. Tl is well known as one of valence-skip elements [6]. The saturation of hole density above x_c has been interpreted in terms of the onset of a degeneracy of impurity states with a formal valence of Tl^{1+} (hole doping) and Tl^{3+} (electron doping) [2–4, 7]. The logarithmic upturn in the temperature (T) dependence of resistivity is observed at low temperatures above x_c. This Kondo-like scattering appears in the absence of unpaired spins [4,8]. These results could be interpreted as evidence for a charge Kondo effect arising from the interaction of conduction electrons with the two degenerate valence states of the Tl dopants (Tl^{1+} and Tl^{3+}) [4, 9–13]. The fact that a logarithmic upturn in the resistivity at low temperatures is observed only in SC samples with $x \geq 0.3\%$ implies that valence fluctuations might play a key role in the SC pairing interaction in $Pb_{1-x}Tl_xTe$ [4, 14]. From the previous Te-NMR measurement in $Pb_{1-x}Tl_xTe$, a

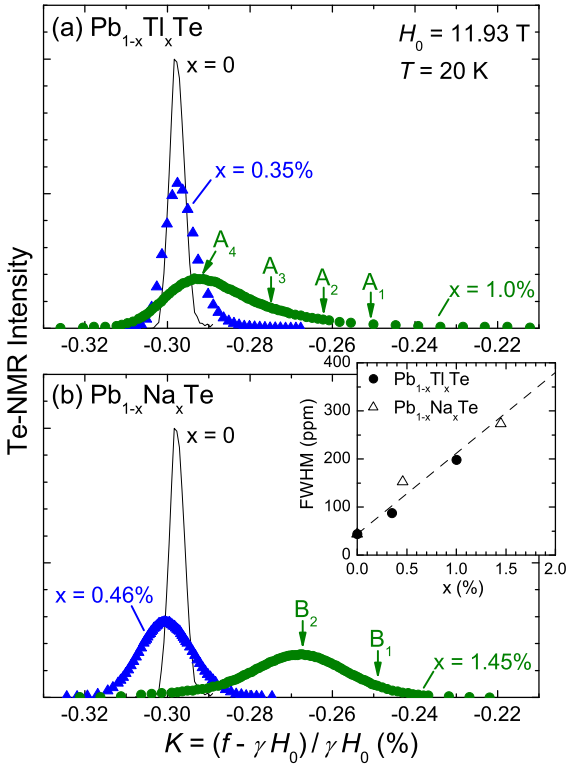

Fig. 1. (a) ^{125}Te-NMR spectra in in $Pb_{1-x}Tl_xTe$ at T = 20 K and $H_0 \sim 12$ T for x = 0, 0.35, and 1.0 %. The $1/T_1T$ data in Fig. 2a are measured at the Te sites denoted by A_i (i = 1 to 4). (b) ^{125}Te-NMR spectra in in $Pb_{1-x}Na_xTe$ at T = 20 K and $H_0 \sim 12$ T for x = 0, 0.46, and 1.45 %. The $1/T_1T$ data in Fig. 2b are measured at the Te sites denoted by B_i (i = 1, 2). The inset shows the x dependence of the full width at half maximum (FWHM) of Te-NMR spectrum in Tl- and Na-doped PbTe compounds.

remarkable increase in $1/T_1T$ in the SC sample with $x = 1.0\%$ is observed upon cooling below 10K for the Te sites close to the Tl dopants, indicating the growth of valence fluctuations at low temperatures [15]. The recent theoretical works reported that the observed enhancement in $1/T_1T$ below 10 K can be readily understood within the charge Kondo picture as the result of the T dependence of the electron-pair hopping interaction J_{ph} between $6s$ pair electrons on the Tl dopants and the conduction electrons [12, 16]. However, it is possible that an increase in Te-$1/T_1T$ is not associated with valence fluctuations between Tl^{1+} and Tl^{3+}. A small amount of some impurity could induce the enhancement of $1/T_1T$ at low temperatures. In order to clarify the origin of an increase in $1/T_1T$, we need a Te-NMR measurement in a non-valence skipping element doped sample. Here, we present a Te-NMR study of hole-doped PbTe in which we use a series of non-superconducting, non-valence skipping Na(Na^{1+})-doped samples.

High-quality single crystals of $Pb_{1-x}Tl_xTe$ (x = 0, 0.35, and 1.0%) and $Pb_{1-x}Na_xTe$ (x = 0.45, and 1.46%) were grown by an unseeded physical vapor transport method, as described previously [4]. They were crushed into coarse powder in order to allow RF pulses to easily penetrate the sample and gain large NMR signals. The ^{125}Te-NMR ($I = 1/2$) spectrum and nuclear spin-lattice relaxation rate ($1/T_1$) were obtained in a magnetic field of $H_0 \sim 11.93$ T. T_1 was measured by the conventional saturation-recovery method with a recovery curve [$R(t) = 1 - M(t)/M_0 = \exp(-t/T_1)$] for $I = 1/2$, where M_0 and $M(t)$ are the nuclear magnetizations for a thermal equilibrium condition and at time t after a saturation pulse, respectively.

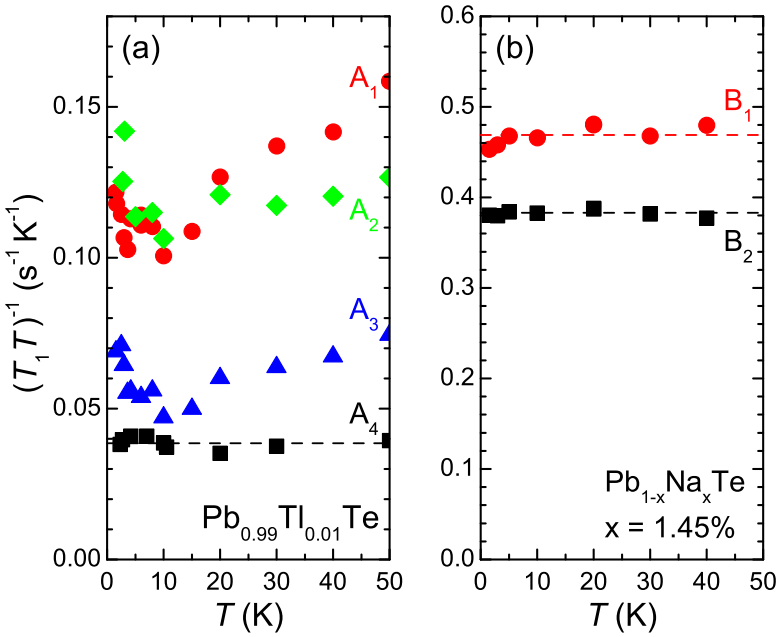

Fig. 2. (a) T dependence of $1/T_1T$ for $Pb_{0.99}Tl_{0.01}Te$ measured at K denoted as A_i (i = 1 to 4) in Fig.1a. (b) T dependence of $1/T_1T$ for $Pb_{1-x}Na_xTe$ with x = 1.45% measured at K denoted as B_i (i = 1, 2) in Fig. 1b. Dashed lines in both Fig. 2a and 2b are eye guides.

2. Experiments and discussion

Figure 1a and 1b show ^{125}Te-NMR spectra in $Pb_{1-x}Tl_xTe$ and $Pb_{1-x}Na_xTe$, respectively. The horizontal axes of Fig. 1a and 1b correspond to Knight Shift (K), which is expressed as $K = (f - \gamma_n H_0)/\gamma_n H_0$. Here, γ_n and f are a nuclear gyromagnetic ratio and NMR frequency, respectively. In Tl-doped PbTe compounds, their spectral width gradually increases with doping impurities of Tl. As shown in the inset of Fig. 1b, the full width at half maximum (FWHM) of Te-NMR spectrum linearly increases with increasing x, indicating that Tl dopants are randomly distributed in the crystals. As shown in Fig. 1a, the peak position of ^{125}Te-spectrum shifts to higher frequency (higher K) by Tl doping in addition to the spectral broadening. In general, K comprises a spin shift K_s and a chemical shift K_{chem}. Since K_{chem} is independent of x in a small range, the peak shift to higher K corresponds to the increase in K_s. K_s is proportional to $A_{hf}\chi_0 \propto A_{hf}N_0$, where χ_0 is a static spin susceptibility at $q = 0$, A_{hf} is a hyperfine coupling constant, and N_0 is density of states (DOS) at the Fermi level (E_F). Therefore, the peak shift to higher K with doping Tl means the increase in DOS. Since the spectral peak shifts to higher K with increasing x, it is probable that the high-K and low-K sides in the Te-NMR spectrum corresponds to Te sites near and far from Tl dopants, respectively. The large distribution of K_s with increasing x is indicative of a strong spatial variation in the local DOS surrounding each Tl dopant. The large enhancement of DOS is locally induced in the vicinity of Tl dopants in $Pb_{0.99}Tl_{0.01}Te$. As shown in Fig. 1b, the spectral broadening by doping impurities is observed in Na-doped PbTe compounds as well as Tl-doped PbTe ones. The FWHM of Te-NMR spectrum in Na-doped PbTe is plotted in the inset of Fig. 1b with that in Tl-doped PbTe ones. Both of them show a simlar linear positive relation with x, indicating that Na dopants are also randomly ditributed in the crystals. The peak position of the Te-NMR spectrum in $Pb_{1-x}Na_xTe$ with $x = 0.46\%$ shifts to slightly lower K. The origin for the peak shift to lower K is so far unknown. However, the spectral peak position in $Pb_{1-x}Na_xTe$ with $x = 1.45\%$ is more largely shifted to higher K than that in $Pb_{0.99}Tl_{0.01}Te$. The spectral broadening and peak shift to higher K suggests the large enhancement of

local DOS surrounding each Na dopant in $Pb_{1-x}Na_xTe$ with $x = 1.45\%$ as well as in $Pb_{0.99}Tl_{0.01}Te$. In the case of Tl doping, two valence states of Tl^{1+}(hole doping) and Tl^{3+}(electron doping) are degenerate for $x > x_c$ ($\sim 0.3\%$), leading to the suppression of carrier doping. However, Na is not a valence-skipping element. Only Na^{1+} is doped into the $Pb_{1-x}Na_xTe$ crystals and the increase in hole concentration is not suppressed by Na doping with $x > 0.3\%$. Therefore, the Te-NMR spectrum in $Pb_{1-x}Na_xTe$ with $x = 1.45\%$ is largely shifted to higher K than that in $Pb_{0.99}Tl_{0.01}Te$.

Next, we address the evolution of the local electronic states introduced by the Tl dopants through the ^{125}Te-T_1 measurements. Figure 2a shows the T dependences of $1/T_1T$ in $Pb_{0.99}Tl_{0.01}Te$, which are measured at the Te sites denoted by A_i ($i = 1$ to 4) in Fig. 1a. It should be noted that the values of K are widely distributed over the sample, which allows us to examine the local electronic characteristics at the different distances from the Tl dopants. In particular, we find that $1/T_1T$ becomes progressively larger for larger values of K. In the case of undoped PbTe, $1/T_1$ has a homogeneous value for all Te sites [15]. The large values of $(1/T_1T)$ at the large values of K originate from the Te sites in the vicinity of the Tl dopants, which is indicative of a significant change in the local electronic state induced by doping Tl atoms. These results demonstrate that the existence of Tl dopants increases the distributions in $(1/T_1T)$ and K with increasing x (> 0). Such an enhancement of the distributions in $(1/T_1T)$ and K by the impurity doping is also observed in Na-doped PbTe. Fig. 2b shows the T dependences of $1/T_1T$ in $Pb_{1-x}Na_xTe$ with $x = 1.45\%$, which are measured at the Te sites denoted by B_i ($i = 1, 2$) in Fig. 1b. The large $1/T_1$ is observed at the large values of K, indicating the enhancement of a local DOS in the vicinity of Na dopants. It should be noted that both Tl- and Na-doping induce a significant change in the local electronic state around dopants.

We discuss the characteristics of valence fluctuations from the T_1 measurements at low T. As shown in Fig. 2a, the enhancement of $1/T_1T$ measured at K denoted as A_i ($i = 1$ to 3) in the vicinity of Tl dopants is observed below 10 K in $Pb_{0.99}Tl_{0.01}Te$. In contrast, $1/T_1T$ measured at K denoted as A_4 far from Tl dopants stays almost constant. These results suggests that the enhancement of $1/T_1T$ below 10 K at Te sites in the vicinity of Tl dopants is induced by valence fluctuations between Tl^{1+} and Tl^{3+}. However, it is possible that some impurity induces the enhancement of $1/T_1T$. In some cases of slightly doped semiconductors, a Curie-Weiss-like T dependence of $1/T_1T$ was observed at low fields due to the magnetization of the impurity states, but they are suppressed by high fields ($H_0 \sim 12$ T in the present NMR measurement) [17–19]. In order to more clarify the cause for the enhancement of $1/T_1T$ below 10 K, we need to compare the T dependences of $1/T_1T$ at low T in valence-skipping Tl-doped and non-valence-skipping Na-doped PbTe compounds. In $Pb_{1-x}Na_xTe$ with $x = 1.45\%$, $1/T_1T$ stays almost constant from $T = 1.8$ to 50 K at Te sites both near and far from Tl dopants, indicating that non-valence-skipping impurities (Na dopants) cannot enhance $1/T_1T$ at low T. These results demonstrate that the enhancement of $1/T_1T$ below 10 K in $Pb_{0.99}Tl_{0.01}Te$ is induced by valence fluctuations associated with the charge Kondo effect arising from Tl dopants.

3. Conclusion

Systematic measurements of the ^{125}Te-NMR spectrum and $1/T_1T$ on $Pb_{1-x}Tl_xTe$ and $Pb_{1-x}Na_xTe$ have revealed that Tl and Na dopants induce spatially inhomogeneous electronic states around those dopants. In the SC sample $Pb_{0.99}Tl_{0.01}Te$, a remarkable increase in $1/T_1T$ is observed upon cooling below 10 K for the Te sites near Tl dopants. Meanwhile, no enhancement of $1/T_1T$ is observed at low T for the Te sites both near and far from non-valence-skipping Na dopants in $Pb_{1-x}Na_xTe$ with $x = 1.45\%$. These results demonstrate that the enhancement of $1/T_1T$ below 10 K can be induced by valence fluctuations associated with the charge Kondo effect arising from Tl dopants. Such an anomaly below 10 K was not detected in non-SC $Pb_{1-x}Na_xTe$ compounds with $x = 0$ and 0.35%. It is possible that the valence fluctuation arising from Tl dopants observed by the present Te-NMR measurements is closely related with the onset of SC or the increase of T_c in $Pb_{1-x}Tl_xTe$.

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