

# Hybridization-driven gap in $U_3Bi_4Ni_3$ : A $^{209}Bi$ NMR/NQR study

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We report  $^{209}Bi$  nuclear-magnetic-resonance and nuclear-quadrupole-resonance measurements on a single crystal of the Kondo insulator  $U_3Bi_4Ni_3$ . The  $^{209}Bi$  nuclear-spin-lattice relaxation rate ( $T_1^{-1}$ ) shows activated behavior and is well fit by a spin gap of 220 K. The  $^{209}Bi$  Knight shift ( $\mathcal{K}$ ) exhibits a strong temperature dependence arising from  $5f$  electrons, in which  $\mathcal{K}$  is negative at high temperatures and increases as the temperature is lowered. Below 50 K,  $\mathcal{K}$  shows a broad maximum and decreases slightly upon further cooling. Our data provide insight into the evolution of the hyperfine fields in a fully gapped Kondo insulator based on  $5f$  electron hybridization.

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## I. INTRODUCTION

Strong electron correlations arising from the interactions between localized spins and conduction electrons are the origin of the unusual physical properties of heavy fermion systems.<sup>1</sup> Among them, Kondo insulators (or heavy fermion semiconductors) are characterized by the emergence of a novel ground state with a small gap driven by the hybridization between the localized  $f$  electrons and the conduction electrons.<sup>2-4</sup> Typically, these materials exhibit behavior similar to other heavy fermion metals at high temperatures and are well described by the single impurity Kondo model. However at low temperature, the semiconducting or insulating behavior arises as a result of the periodic array of the local moments and can be described by the periodic Anderson model. In a Kondo insulator, the chemical potential lies within the gap driven by the hybridization, leading to an insulating behavior at sufficiently low temperatures.

Whereas there are a number of rare-earth-( $4f$ ) based Kondo insulators, which include  $Ce_3Bi_4Pt_3$ ,<sup>5,6</sup>  $CeRhPn$  ( $Pn = As, Sb$ ),<sup>7</sup>  $SmB_6$ ,<sup>8</sup> and  $YbB_{12}$ ,<sup>9</sup> actinide-based Kondo insulators are less well studied. To date, there are reports of Kondo insulating behavior in  $U_3Sb_4X_3$  ( $X = Ni, Pt, Pd$ ) and  $U_2Ru_2Sn$ .<sup>10-14</sup> The recently discovered uranium ternary compound  $U_3Bi_4Ni_3$  is another potential candidate<sup>15</sup> that might be considered as the uranium counterpart of the well-known Kondo insulator  $Ce_3Bi_4Pt_3$ . These compounds are not only isostructural but also isoelectronic assuming the valance state of U is  $>3+$  but  $<4+$ .  $U_3Bi_4Ni_3$  has a body-centered-cubic  $Y_3Sb_4Au_3$ -type structure with the lattice parameter  $a = 9.5793 \text{ \AA}$  (space group:  $I\bar{4}3d$ ). In this crystal structure, the U and Ni atoms occupy unique crystallographic sites with fourfold inversion symmetry. The single Bi site [16(c)] has a threefold axial symmetry along the [111] direction. Each Bi atom has three U (and Ni) nearest neighbors that form an equilateral triangle on a plane perpendicular to its axis of symmetry.<sup>15</sup> A fully gapped ground state was inferred by specific-heat and photoemission measurements,<sup>15</sup> in which specific heat showed a Sommerfeld coefficient  $\gamma_0 \sim 0$  and the photoemission measurements revealed an electronic gap of

840 K. However, because  $Th_3Bi_4Ni_3$ , which is nonmagnetic with  $Th^{4+}$ , is also an insulator, these initial studies were unable to establish the origin of the gapped state in  $U_3Bi_4Ni_3$ .

In this paper, we report  $^{209}Bi$  nuclear-magnetic-resonance (NMR) and nuclear-quadrupole-resonance (NQR) results on a single crystal of  $U_3Bi_4Ni_3$ . The high-temperature magnetic susceptibility exhibits Curie-Weiss behavior, with an effective moment of  $3.44\mu_B$  consistent with either a  $5f^2$  ( $U^{4+}$ ) or  $5f^3$  ( $U^{3+}$ ) electronic configuration at the U site. The Weiss temperature  $\Theta = -117 \text{ K}$  suggests the presence of antiferromagnetic correlations, yet the ground state is nonmagnetic. In fact, the suppression of  $\chi$  from the Curie-Weiss behavior at low temperature is consistent with the presence of a hybridization gap. The  $^{209}Bi$  Knight shift  $\mathcal{K}$  scales linearly with the magnetic susceptibility  $\chi$  down to a temperature  $T^* \sim 100 \text{ K}$ . Below this temperature, we find a Knight-shift anomaly which differs from that observed in the isostructural  $Ce_3Bi_4Pt_3$  Kondo insulator. We also find that the electric field gradient (EFG) as probed by the nuclear quadrupole frequency  $\nu_Q$  exhibits a strong  $T$  dependence, which probably reflects a decrease in the unit-cell volume. The strongest evidence for the presence of a gap is found in the spin-lattice relaxation rate  $T_1^{-1}$ , which exhibits Arrhenius behavior between 25 and 150 K. We find an activation energy of 220 K, which we identify with the hybridization gap.

## II. SAMPLE PREPARATION AND EXPERIMENTAL DETAILS

Single crystals of  $U_3Bi_4Ni_3$  were grown as described in detail in Ref. 15.  $^{209}Bi$  (nuclear spin  $I = 9/2$ ) NMR and NQR were performed using a conventional phase-coherent-pulsed spectrometer. Knight-shift measurements were carried out at the central transition of the  $^{209}Bi$  at 29 MHz ( $\sim 4.2 \text{ T}$ ). The temperature dependence of the nuclear quadrupole frequency ( $\nu_Q$ ) and the nuclear-spin-lattice relaxation rate  $T_1^{-1}$  were measured in zero field (NQR). The Bi atoms are located at axially symmetric sites, and thus the NQR spectrum consists of four equally spaced transitions.  $T_1^{-1}$  was measured by the saturation recovery at the highest NQR transition  $4\nu_Q$

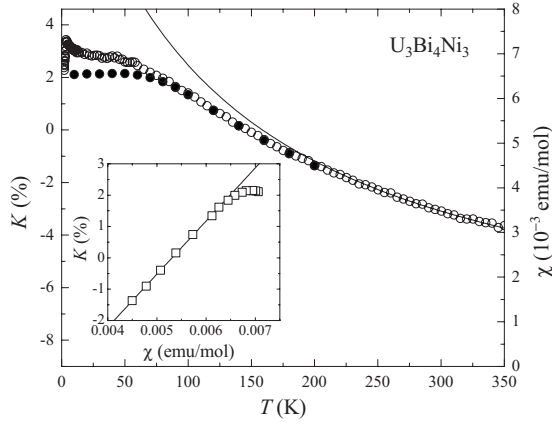


FIG. 1. Magnetic susceptibility ( $\circ$ )  $^{209}\text{Bi}$  Knight shift  $\mathcal{K}$  ( $\bullet$ ) as a function of temperature in a single crystal of  $\text{U}_3\text{Bi}_4\text{Ni}_3$ . The susceptibility was measured at 0.1 T. The sharp decrease of  $\chi$  below 3.5 K is attributed to the small amount of superconducting BiNi on the surface. The solid curve is a Curie-Weiss fit, as discussed in the text. The inset shows  $\mathcal{K}$  versus  $\chi$ . The solid line is a linear fit to the high-temperature data, yielding a hyperfine coupling constant  $A_{\text{hf}} = 94(5)$  kOe/ $\mu_B$  and temperature-independent shift  $\mathcal{K}_0 = -9(0.3)\%$ . Below  $T^* \approx 100$  K, the linear relationship breaks down.

$= 38.13$  MHz ( $\pm \frac{7}{2} \leftrightarrow \pm \frac{9}{2}$ ). The relaxation data was then fit to the following equation appropriate for this transition:

$$1 - \frac{M(t)}{M(\infty)} = \frac{16}{715} \exp\left(-\frac{36t}{T_1}\right) + \frac{49}{165} \exp\left(-\frac{21t}{T_1}\right) + \frac{80}{143} \exp\left(-\frac{10t}{T_1}\right) + \frac{4}{33} \exp\left(-\frac{3t}{T_1}\right). \quad (1)$$

### III. RESULTS AND DISCUSSION

#### A. Magnetic susceptibility and Knight shift $\mathcal{K}$

Figure 1 shows the magnetic susceptibility  $\chi$  measured at 0.1 T. For temperatures above 250 K, a Curie-Weiss fit yields a magnetic moment of  $3.44\mu_B$  and a Weiss temperature  $\Theta = -117$  K. As seen in the figure and in the inset,  $\mathcal{K}$  tracks the bulk susceptibility  $\chi$  down to approximately 100 K, and below 100 K, the Knight shift passes through a weak maximum. Plotting  $\mathcal{K}$  versus  $\chi$ , we obtain the hyperfine coupling constant  $A_{\text{hf}} = 94(5)$  kOe/ $\mu_B$  and the temperature-independent shift  $\mathcal{K}_0 = -9(0.3)\%$ .  $\mathcal{K}_0$  most likely represents both orbital and Van Vleck contributions to the magnetic susceptibility of the U atoms; whereas the remaining temperature-dependent part reflects the contribution from local  $5f$  moments. As a result of the hybridization between the  $5f$  electrons and the itinerant conduction electrons, the linear  $\mathcal{K}$ - $\chi$  relationship breaks down below  $T^* \approx 100$  K, as observed in a number of other heavy fermion compounds.<sup>16</sup> This Knight-shift anomaly arises because there are different hyperfine couplings to the conduction-electron spins  $S_c$  and to the  $f$ -electron spins  $S_f$ . Below a characteristic temperature  $T^*$ , which reflects the scale of the intersite correlations, the correlation function  $\chi_{\text{cf}} = \langle S_c S_f \rangle$  begins to dominate the susceptibility and gives rise to the difference between  $\mathcal{K}$  and  $\chi$ .

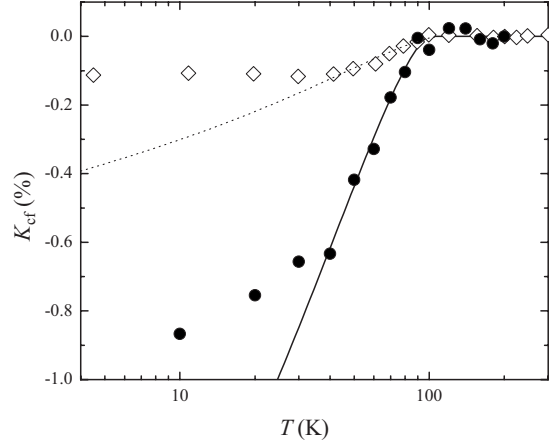


FIG. 2.  $K_{\text{cf}}$  versus  $T$  in  $\text{U}_3\text{Bi}_4\text{Ni}_3$  ( $\bullet$ ) and in  $\text{Ce}_3\text{Bi}_4\text{Pt}_3$  ( $\diamond$ ). The solid and dotted lines are fits as described in the text.

In Fig. 2 we plot the difference  $K_{\text{cf}} = \mathcal{K} - \mathcal{K}_0 - A\chi$  versus temperature and compare with that observed in  $\text{Ce}_3\text{Bi}_4\text{Pt}_3$ . The solid and dotted lines are fits to the two-fluid expression  $K_{\text{cf}} = K_{\text{cf}}^0 (1 - T/T^*)^{3/2} [1 + \log(T^*/T)]$  with  $T^* = 100(3)$  K for  $\text{U}_3\text{Bi}_4\text{Ni}_3$  and  $T^* = 110(5)$  K for  $\text{Ce}_3\text{Bi}_4\text{Pt}_3$  that has been used successfully in several other heavy fermion compounds.<sup>17</sup> In both cases,  $|K_{\text{cf}}|$  grows with decreasing temperature below  $T^*$ , reflecting the growth of correlations, yet below approximately 40 K,  $K_{\text{cf}}$  no longer scales with the universal behavior observed in other heavy fermions. The origin of this discrepancy is not known; but we speculate that in the Kondo insulating state there are no excited heavy quasiparticles and hence  $\chi_{\text{cf}}$  is modified. The fact that  $\mathcal{K}$  saturates at a finite value at low temperature strongly suggests that a hyperfine field due to the  $5f$  electron spins remains present in the hybridized insulating state.

#### B. Electric field gradient

For nuclei with spin  $I > 1/2$ , the nuclear quadrupole moment  $Q$  interacts with the surrounding EFG, lifting the degeneracy of the multiplet in zero field. If the nucleus sits in a site with axial symmetry (and lower than cubic) then the quadrupolar Hamiltonian is given by

$$\mathcal{H} = \frac{e^2 q Q}{4I(2I-1)h} [3I_z^2 - I^2]. \quad (2)$$

In this case the splitting between adjacent sublevels  $\pm m$  and  $\pm(m+1)$  is given by  $(m+1/2)\nu_Q$ , where  $\nu_Q = 3e^2 q Q / [I(2I-1)h]$  is the NQR frequency,  $m$  is the  $I_z$  eigenvalue,  $h$  is Planck's constant,  $e$  is the electron charge, and  $q$  is the principal eigenvalue of the EFG tensor.<sup>18</sup> In  $\text{U}_3\text{Bi}_4\text{Ni}_3$ , the  $^{209}\text{Bi}$  nucleus has  $I = 9/2$  and sits in an axially symmetric site (16c) (see inset of Fig. 3). We find three well-separated NQR lines at the frequency of  $n\nu_Q$  with  $n = 2, 3, 4$  and  $\nu_Q = 9.531$  MHz at low temperature. As expected, our results are consistent with the axial symmetry (anisotropy parameter  $\eta = 0$ ). Figure 3 shows the temperature dependence of  $\nu_Q$  measured at the  $4\nu_Q$  transition, in which  $\nu_Q$  increases with decreasing temperature and reaches a plateau below 100 K.

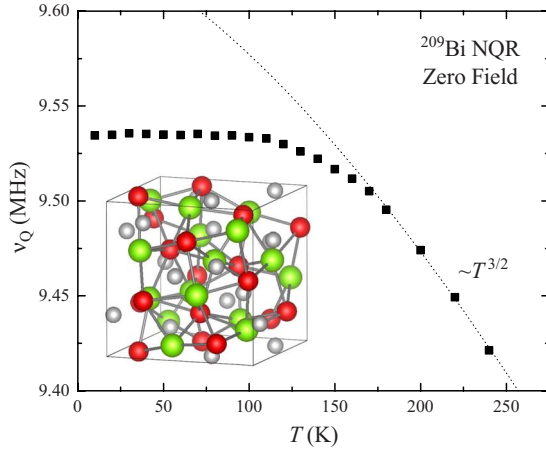


FIG. 3. (Color online)  $^{209}\text{Bi}$  nuclear quadrupole frequency  $\nu_Q$  as a function of temperature. Above 200 K,  $\nu_Q$  increases with decreasing  $T$ , as expected from the phonon contribution  $\propto T^{3/2}$  (dotted line).  $\nu_Q$  bends over to a constant value below  $\sim 170$  K. Inset: the  $U_3Bi_4Ni_3$  structure. The red (middle-size) atoms represent U, the green (large) atoms represent Bi, and the gray (small) atoms represent Ni.

There are two principle contributions to the EFG: the on-site asymmetric orbitals and the off-site charges in the lattice. In most solids, the temperature dependence arises from the lattice vibrations (phonons) in which the phenomenological relation  $\nu_Q \propto T^{3/2}$  generally holds.<sup>19</sup> In fact, we find  $\nu_Q \sim T^{3/2}$  down to roughly 170 K, as shown in Fig. 3. However, below this temperature,  $\nu_Q$  acquires a different temperature dependence. We find that the suppression of  $\nu_Q$  is qualitatively similar to that of the isostructural  $Ce_3Bi_4Pt_3$ . If we adopt the same analysis as made in Ref. 20, the suppression of  $\nu_Q$  at low  $T$  can be ascribed to the change in the lattice parameter. In this case,  $\nu_Q$  may be written as the following form:

$$\nu_Q = \nu_Q^0 - a/V(T) - bT^{3/2}, \quad (3)$$

where  $V$  is the cell volume,  $\nu_Q^0$  is the temperature-independent term, and  $a, b$  are the positive constants. In this case, our data suggest that below 170 K, the cell volume  $V(T)$  decreases with decreasing temperature. Although there is no available data of the lattice parameter at low temperatures yet, we suggest that this apparent decrease in the cell volume is related to the onset of hybridization of  $5f$  electrons with the conduction band. This onset correlates well with our Knight-shift measurements showing  $T^* \sim 100$  K.

### C. Nuclear-spin-lattice relaxation rate

The nuclear-spin-lattice relaxation rate  $T_1^{-1}$  is shown as a function of  $T$  in Fig. 4.  $T_1^{-1}$  drops dramatically between 150 and 25 K and is well fit by an Arrhenius expression  $T_1^{-1} = A \exp(-\Delta/T)$ , with  $\Delta = 220(10)$  K. This result reveals the gapping of excited quasiparticles at low temperature, in agreement with resistivity measurements that show this material to be nonmetallic and specific-heat measurements that reveal a vanishing Sommerfeld coefficient.<sup>15</sup> We would not expect these behaviors to arise from only depopulation of an

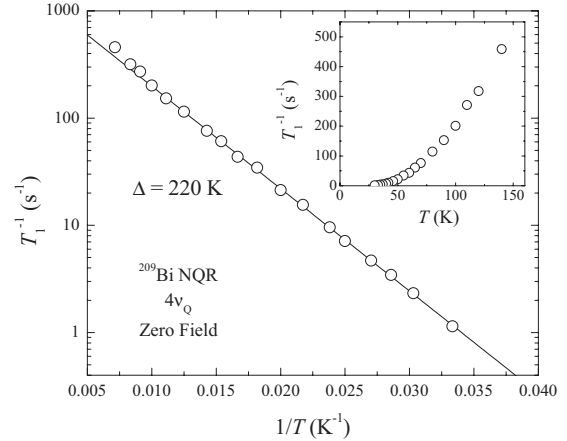


FIG. 4.  $T_1^{-1}$  of  $^{209}\text{Bi}$  NQR in zero field measured at  $4\nu_Q$  line.  $T_1^{-1}$  versus  $1/T$  plot reveals the activation behavior with the single activation energy  $\Delta = 220$  K. Inset shows that  $T_1^{-1}$  decreases exponentially with decreasing temperature.

excited crystal-field level such as found in  $U_3Sb_4Ni_3$ .<sup>21</sup> Furthermore, the high quality of the Arrhenius fit rules out the possibility of an impurity band near the chemical potential. Photoemission results have revealed a gap in the density of states of 840 K,<sup>15</sup> roughly four times the gap measured by NMR. The origin of this difference is not clear but may be related to spin versus charge excitations. Similar results were found in  $Ce_3Bi_4Pt_3$  (Ref. 20), and we argue that this behavior is a signature of a Kondo insulating ground state in  $U_3Bi_4Ni_3$ . It is curious that the Knight shift reveals a large hyperfine field at low temperatures, whereas  $T_1^{-1}$  indicates the absence of any substantial fluctuating hyperfine fields. *A priori*, these results appear somewhat contradictory, as the same hyperfine field is responsible for both phenomena. However, if the electronic system is described by a periodic Anderson lattice with two dispersing bands of partial  $f$  character and a chemical potential lying in the hybridization gap then at low temperature it is possible that the occupied lower band may consist of a significant  $f$  character that will contribute to a static magnetization. Scattering of heavy-mass quasiparticles, on the other hand, will not be present for temperatures much less than the gap value.

We note that this gap value is smaller than the value reported in Ref. 15 but still larger than the gap values of most Ce-based Kondo insulators.<sup>4</sup> This difference between the  $4f$  and  $5f$  gap values may indicate the better hybridization between U  $5f$  electrons and conduction electrons from Bi  $6p$  and/or Ni  $3d$  bands in  $U_3Bi_4Ni_3$ . We note that  $T^*/\Delta \sim 0.48$  for  $U_3Bi_4Ni_3$ , whereas  $T^*/\Delta \sim 0.61$  for  $Ce_3Bi_4Pt_3$ . The origin of this discrepancy is unclear but suggests that the energy scales determining  $\Delta$  ( $T_K$ ) and  $T^*$  differ, as argued recently in Ref. 17.

## IV. CONCLUSION

We presented  $^{209}\text{Bi}$  NMR/NQR measurements on a single crystal of  $U_3Bi_4Ni_3$ . Knight-shift and susceptibility measurements reveal a Knight-shift anomaly that probably arises due to different hyperfine couplings to the  $5f$  electron spins and

to the itinerant conduction electrons. The Knight-shift anomaly is in reasonable agreement with the two-fluid model and is similar with observations in  $\text{Ce}_3\text{Bi}_4\text{Pt}_3$ .<sup>20</sup> The temperature dependence of the EFG suggests a reduction in the unit-cell volume at low temperatures and may be related to the onset of hybridization between the lattice of nearly localized  $5f$  electrons and the conduction band. The most striking result is the spin-lattice relaxation rate, which exhibits activated behavior between 150 and 25 K, with an activation energy  $\Delta=220$  K. Our results suggest that  $\text{U}_3\text{Bi}_4\text{Ni}_3$  is a  $5f$ -based Kondo insulator and that strong correlations play an important role in this structural class of U-based compounds.

Detailed electronic structure calculations should help to shed light on the role of correlations in these materials. Finally, our results provide constraints on the interpretation of NMR in  $f$ -electron systems in the limit of vanishing quasiparticles.

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