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Evidence for an antiferroquadrupolar ordering in YbSb probed by ^{121}Sb and ^{123}Sb nuclear magnetic resonances

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Formation of the antiferroquadrupolar (AFQ) ordering in YbSb (NaCl-type structure) was evidenced microscopically with the ^{121}Sb and ^{123}Sb nuclear magnetic resonance (NMR) measurements. We have observed in the NMR linewidth below $T_Q=5$ K the appearance of an additional field-independent contribution that is proportional to the nuclear electric-quadrupole moment. Thus, the field-independent contribution can be addressed not to any long-range magnetic orderings but to a broken symmetry of the charge distribution associated with the AFQ ordering. The AFQ ordering also gives rise to a large anisotropic Knight shift broadening caused by the anisotropy in the transferred hyperfine field and/or magnetic susceptibility. Fluctuations of the Yb $4f$ moments are also investigated by using the $^{121,123}\text{Sb}$ spin-lattice relaxation rate measurements.

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Long-range ordering involving orbital degrees of freedom in transition-metal and rare-earth compounds is at the forefront of physics of the strongly correlated electron system. In contrast to transition-metal ions, lanthanide ions are characterized by the strong coupling between the total spin and orbital momenta, which rules out the pure orbital ordering. When the orbital degeneracy is not quenched out, however, it has been known that interactions between multipole (especially quadrupole) moments of the f -electron wave functions play a significant role on low-temperature physical properties,¹ and even lead to a long-range ordered state² in such as Ce and U compounds.^{3,4}

Low-carrier heavy-fermion ytterbium-monopnictides YbX ($X=\text{N}, \text{P}, \text{As}, \text{Sb}$) with a NaCl-type crystal structure have attracted much interest because of their unusual properties originating from the competition between the Kondo hybridization and the Ruderman-Kittel-Kasuya-Yosida (RKKY) interactions.⁵ Neutron diffraction and Mössbauer measurements showed that YbN, YbP, and YbAs have similar magnetic properties: antiferromagnetic (AFM) ordering with almost the same transition temperatures of about 0.5 K, and magnetic moments of about half of $1.33\mu_B$ expected for the crystalline electric field (CEF) ground state Γ_6 .^{6,7}

For YbSb, on the other hand, Mössbauer,⁸ specific heat,⁹ and nuclear magnetic resonance (NMR)^{10,11} measurements reported the presence of two distinct phase transitions of the AFM ordering at 0.32 K and a possible antiferroquadrupolar (AFQ) ordering at 5 K. The CEF ground state of the Γ_6 Kramers doublet has no quadrupole moment. Hashi *et al.*⁹ discussed the phase transition at 5 K in terms of a mixing-typed AFQ ordering model¹² with interactions between the ground state Γ_6 and excited state Γ_8 of Yb³⁺ ions. However, the phase transition at 5 K has been less studied experimentally and is not yet well established. In this study, we have performed ^{121}Sb and ^{123}Sb -NMR measurements to elucidate the phase transition microscopically.

A stoichiometric polycrystalline sample of YbSb was prepared with a wedgetype cubic-anvil high-pressure apparatus. X-ray powder diffraction measurements showed that the crystal structure is of NaCl type. The NMR measurement was carried out using a wideband phase-coherent spin-echo spectrometer in a temperature range between 1.4 and 100 K. NMR spectra of ^{121}Sb (gyromagnetic ratio $\gamma_n=1.0189$ kHz/Oe, nuclear spin $I=\frac{5}{2}$, electric quadrupole moment $Q=-0.53$ b) and ^{123}Sb ($\gamma_n=0.55175$ kHz/Oe, $I=\frac{7}{2}$, $Q=-0.68$ b) were obtained in a field sweeping procedure at several constant frequencies in a range between 3.5 and 75 MHz. Above ~ 5 K, $^{121,123}\text{Sb}$ -NMR spectra have a Lorentzian-type line shape, as shown in the inset of Fig. 1. The full width of half maximum (FWHM) is independent of temperature. Lack of any quadrupole splittings (or broadenings) is consistent with the cubic symmetry distribution of

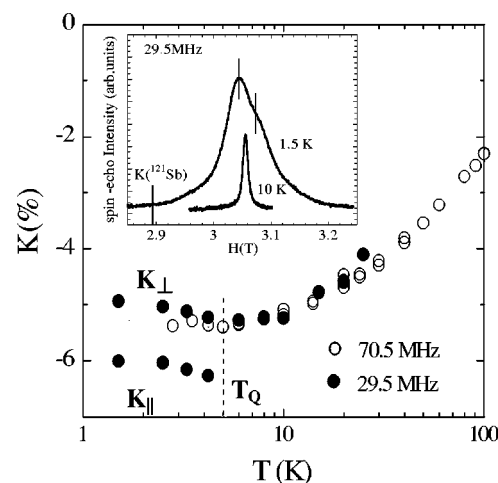


FIG. 1. Knight shift of ^{121}Sb -NMR in YbSb at 29.5 and 70.5 MHz plotted against temperature. Inset of the figure shows typical NMR spectra above and below 5 K.

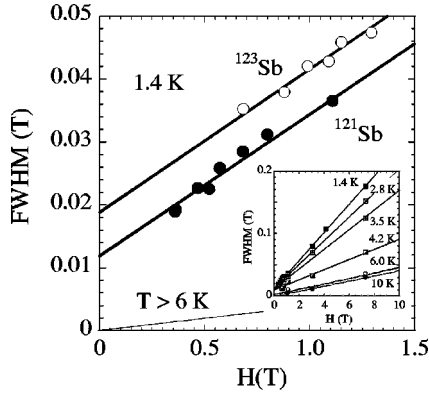


FIG. 2. Full width of half maximum of ^{121}Sb and ^{123}Sb resonance linewidth in YbSb plotted against applied magnetic field.

the ionic charge on the neighboring lattice sites. The Knight shift $K=(H_0-H_{\text{res}})/H_{\text{res}}$ determined at the peak intensity point is plotted in Fig. 1 against temperature. Below ~ 5 K, on the other hand, the $^{121-123}\text{Sb}$ -NMR lines are largely broadened and have an anisotropic line shape (inset of Fig. 1). The Knight shifts K_{\perp} deduced from the peak and K_{\parallel} from the shoulder of the spectra obtained at 29.5 and 70.5 MHz are also plotted in Fig. 1.

We plot in Fig. 2 the FWHM data for each of ^{121}Sb and ^{123}Sb against applied magnetic field H . The important feature is that the FWHM below ~ 5 K consists of a magnetic field-dependent term ΔH_M and a field-independent term ΔH_0 : $\Delta H(H)=\Delta H_M(H)+\Delta H_0$, which is consistent with the ^{121}Sb -NMR data reported previously by Hashi *et al.*¹¹ Values of ΔH_0 can be deduced by extrapolating the linear relationship between the FWHM and applied magnetic field to $H=0$. The results are plotted in the inset of Fig. 3 as a function of temperature. The field-independent contribution ΔH_0 to the linewidth suddenly appears below ~ 5 K, and tends to saturate at lower temperatures. Hashi *et al.* suggested that the appearance of ΔH_0 originates from a magnetic ordering of the Yb moments.¹¹ However, we observed an isotope effect on the ^{121}Sb - and ^{123}Sb -NMR linewidths that does not support this conjecture.

As shown in Fig. 2, ΔH_0 for ^{123}Sb is larger than that for ^{121}Sb , and the isotope ratio $\Delta H_0(^{121}\text{Sb})/\Delta H_0(^{123}\text{Sb}) \approx 0.63$ is near to the nuclear quadrupole moment ratio $Q(^{121}\text{Sb})/Q(^{123}\text{Sb}) \approx 0.78$. Thus we conclude that the field-independent linewidth appeared below ~ 5 K originates from the first-order perturbation on the Zeeman-split nuclear-spin levels by the nuclear-quadrupole interaction between the electric field gradient (EFG) at the Sb nuclei and the quadrupole moment Q . A small ΔH_0 of about 10^2 Oe leads the pure nuclear-quadrupole resonance to a very low frequency that is hard to observe. The saturating behaviors of ΔH_M below ~ 5 K at low frequency (Fig. 3) can be scaled by that of ΔH_0 , indicating that both are dominated by a single-order parameter. The additional small increase in ΔH_M below ~ 5 K observed at high frequency is considered to be a precursor of the AFM ordering at $T_N \approx 0.32$ K. It is worth noting that the value ΔH_M is directly proportional to the applied magnetic field. This also indicates that the large increase in ΔH_M below ~ 5 K is not caused by any long-range magnetic orderings of the Yb moments.

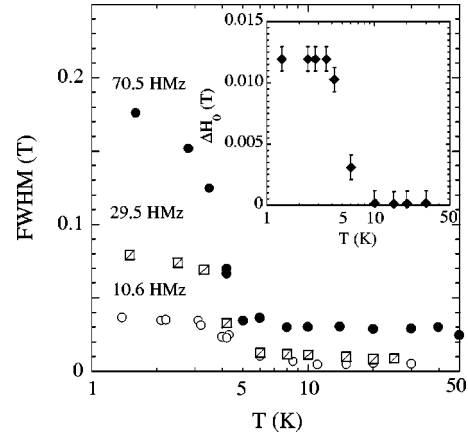


FIG. 3. Full width of half maximum of ^{121}Sb resonance linewidth in YbSb plotted against temperature. Inset is the magnetic field-independent component in the ^{121}Sb resonance linewidth plotted against temperature.

In a cubic crystal structure, the CEF Hamiltonian is expressed as¹³

$$\mathcal{H}_{\text{CEF}} = N[B_4^0(O_4^0 + 5O_6^4) + B_6^0(O_6^0 - 21O_6^4)], \quad (1)$$

where B_j^0 are CEF parameters and O_m^n are Steven's operators. The $J=\frac{7}{2}$ multiplet of Yb^{3+} ion in YbX splits into a ground-state Γ_6 doublet, and two excited states of Γ_8 quartet and Γ_7 doublet.^{9,10,14} The spin degeneracy of the Γ_6 state is considered to be quenched out by the AFM ordering at 0.32 K. The quadrupolar interaction \mathcal{H}_{QO} is given by the squared matrix element,

$$q_{ll'} = \sum |\langle \Gamma_l \gamma | \mathcal{O} | \Gamma_{l'} \gamma' \rangle|^2, \quad (2)$$

of the Γ_3 -type quadrupolar operators,⁹

$$u = J_z^2 - \frac{1}{3}J(J+1),$$

$$v = (J_x^2 - J_y^2)\sqrt{3}, \quad (3)$$

where γ denotes the components of Γ_l . Within the Γ_6 doublet, there is no squared matrix element: $q_{66}=0$. The largest element is a mixing-type coupling between the Γ_6 and Γ_8 states, $q_{68}=q_{86}=70$, which can lead to a quadrupole ordering at low temperatures. The AFQ ordering can, therefore, be caused by the mixing-type coupling between the Γ_6 and Γ_8 states representing the asphericity of the charge distribution. The appearance of the nuclear-quadrupole broadening ΔH_0 below ~ 5 K in the $^{121,123}\text{Sb}$ -NMR spectra and, therefore, the EFG at the Sb site can be caused by this AFQ ordering with a different periodicity from that of the lattice.

At high temperatures above ~ 5 K, the Knight shift of ^{121}Sb is nearly isotropic. The negative value increases with decreasing temperature and takes a maximum near 5 K (Fig. 1). Below ~ 5 K, the ^{121}Sb -NMR spectrum becomes largely anisotropic in shape, and both K_{\parallel} and K_{\perp} turn to decrease with decreasing temperature. Figure 4 shows the dependence of the ^{121}Sb -Knight shift K on the uniform susceptibility χ observed at 50 kOe (shown in the inset). This plot is motivated by the usual expression,

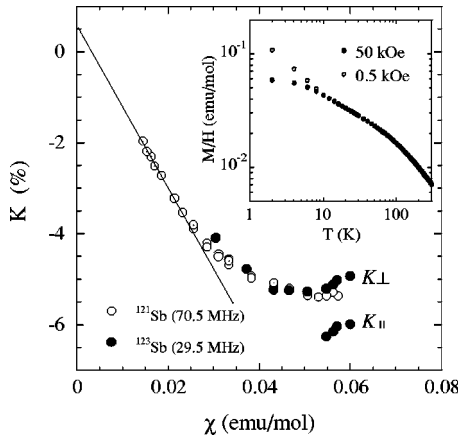


FIG. 4. ^{121}Sb -Knight shift versus susceptibility plots for YbSb obtained at 29.5 and 70.5 MHz. Inset shows the dependence of the magnetization divided by the applied magnetic field.

$K = (\gamma_e \gamma_n \hbar^2)^{-1} A_{hf} \chi$, where $A_{hf}/\gamma_n \hbar$ is the hyperfine field on the observed nucleus.¹⁵ The slope of a straight-line relationship (solid line) obtained above ~ 20 K gives $A_{hf}/\gamma_n \hbar = -10.3 \text{ kOe}/\mu_B$ which is considered to be dominated by the transferred coupling with the Yb^{3+} spins. Below ~ 20 K, the negative shift is smaller than would be predicted from linear extrapolation of the high-temperature data, indicating that the value of A_{hf} decreases with decreasing temperature. The variation of A_{hf} below ~ 20 K is expected if the hyperfine field is anisotropic, since then the Γ_6 ground-state wave function of the Yb^{3+} ion will cause it to couple differently to neighboring Sb nuclei than the Γ_8 excited state.^{16,17} We note that $A_{hf}^6 < A_{hf}^8$ for the experimental decrease in A_{hf} at low temperatures.

As can be seen in the inset of Fig. 2, the uniform susceptibility shows the monotonic increase down to 2 K, indicating that there is no long-range magnetic ordering. On the other hand, we found that the ^{121}Sb -NMR spectrum below ~ 5 K, shows the large anisotropic Knight shift broadening, in addition to the small nuclear-quadrupole broadening. Utilizing the relations $K_{iso} = \frac{1}{3}(K_{\parallel} + 2K_{\perp})$ and $K_{an} = \frac{1}{3}(K_{\parallel} - K_{\perp})$, we obtain the isotropic Knight shift $K_{iso} = -5.29\%$ and anisotropic Knight shift $K_{an} = -0.35\%$ at 1.5 K. K_{an} originates from the anisotropy in A_{hf} and/or χ . The AFQ ordering of the Yb^{3+} ions gives rise to the anisotropy in the hyperfine field. The strong coupling between the total spin and orbital momenta is also expected to cause the anisotropic susceptibility. In the present case of powdered sample, however, we cannot discriminate between these two contributions.

The ^{121}Sb spin-lattice relaxation time T_1 was measured at the peak intensity point of the spectrum, utilizing a radio frequency (rf) single-pulse saturation method. Above ~ 5 K, the magnetization recovery $M(t)$ at time t after the saturation pulse displayed a single-exponential behavior, $M(\infty) - M(t) = M(\infty)e^{-t/T_1}$. This is expected for equally separated nuclear spin levels in energy by the Zeeman interaction. With lowering temperature below ~ 5 K, on the other hand, the magnetization recovery tends to show a multiexponential behavior. For unequally separated nuclear spin levels by the nuclear-quadrupole interaction perturbation, the di-

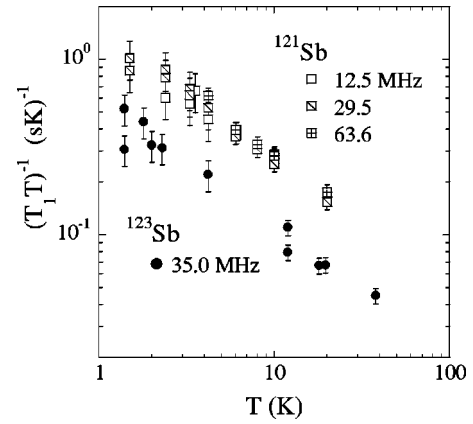


FIG. 5. Temperature dependencies of ^{121}Sb and ^{123}Sb relaxation rates in YbSb.

agonalization of the rate equation gives a magnetization recovery behavior expressed as¹⁸

$$\frac{M(\infty) - M(t)}{M(\infty)} = a_1 e^{-t/T_1} + a_2 e^{-6t/T_1} + a_3 e^{-15t/T_1} + a_4 e^{-28t/T_1}, \quad (4)$$

where the coefficients a_i ($i=1-3$ for ^{121}Sb , and $1-4$ for ^{123}Sb) depend on the initial saturation condition imposed on the nuclear spin levels, and $\sum_i a_i = 1$. The experimental recovery data can be reproduced satisfactorily with Eq. (4), where the value of a_1 decreases rapidly with decreasing temperature. The anisotropy in the hyperfine field and/or susceptibility would give rise to a distribution of the relaxation rate. However, because of the small perturbing rf field H_1 of ≈ 50 Oe when compared with the separation in field between the peak and shoulder of the spectrum, this is not considered to largely affect the experimental recovery curve measured at the peak intensity point. The values of $(T_1 T)^{-1}$ for ^{121}Sb obtained at 12.0, 29.5, and 70.5 MHz are plotted in Fig. 5 against temperature on a log-log scale.

The $(T_1 T)^{-1}$ data for ^{123}Sb measured at 35.0 MHz are also plotted in the figure. The isotope ratio of the relaxation rate $(T_1 T)^{-1}(^{121}\text{Sb})/(T_1 T)^{-1}(^{123}\text{Sb}) \sim 4$ is close to the squared gyromagnetic ratio $\gamma_n^2(^{121}\text{Sb})/\gamma_n^2(^{123}\text{Sb}) = 3.41$. This is an indication that the relaxation of the Sb nuclear spins is dominated not by the quadrupole relaxation $(T_1^{-1})_Q$ but the magnetic relaxation $(T_1^{-1})_M$. On the other hand, Oyamada *et al.* recently reported that $(T_1^{-1})_Q$ becomes effective below 5 K with different temperature dependence from that of $(T_1^{-1})_M$, and ascribed it to the quadrupolar ordering.¹⁹ We think, however, their T_1 data are not convincing, and not consistent with the experimental fact that magnetic linewidth ΔH_M below ~ 5 K at low frequency can be scaled by that of quadrupole linewidth ΔH_0 . The different temperature dependence of ^{121}Sb and ^{123}Sb around 5 K could originate from different initial saturation conditions for the T_1 measurements.

As shown in Fig. 5, $(T_1 T)^{-1}$ is rather insensitive to the magnetic field, and increases with decreasing temperature without displaying any significant change near 5 K, as in the

prototypical quadrupolar ordering compound CeB_6 .²⁰ $(T_1T)^{-1}$ originates from the spin fluctuations is given by

$$(T_1T)^{-1} = \frac{k_B \gamma_n}{2\mu_B^2} \sum_q A_{hf}(q)^2 \text{Im } \chi(q, \omega_0)/\omega_0, \quad (5)$$

where $\chi(q, \omega)$ is the dynamical susceptibility, q the wave vector of spin fluctuations, and ω_0 the NMR frequency. The increasing rate of $(T_1T)^{-1}$ with decreasing temperature is larger than that of the uniform susceptibility $\chi(0, 0)$ (inset of Fig. 4). Taking the decrease in A_{hf} at low temperatures into account, this suggests that the staggered susceptibility $\chi(Q_{AF}, 0)$ originating from the $4f$ moments largely increases

with decreasing temperature, which is consistent with the formation of the AFQ ordering with $q \approx Q_{AF}$. The fluctuation behavior of the Yb^{3+} moments in the AFQ ordered state is quite interesting and calls for further detailed T_1 measurement.

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