Spin-Triplet Superconductivity in UNi_2Al_3 Revealed by the ^{27}Al Knight Shift Measurement

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We report ^{27}Al Knight shift (^{27}K) measurement on a single-crystal UNi_2Al_3 that reveals a coexistence of superconductivity and a spin-density-wave (SDW) type of magnetic ordering ($T_{SDW} = 4.5$ K). The spin part of ^{27}K, $^{27}K_s$, does not change down to 50 mK across the superconducting (SC) transition temperature $T_c \sim 0.9$ K. In contrast with the isostructural compound UPd_2Al_3 ($T_c \sim 2$ K), which was identified to be a spin-singlet d-wave superconductor, the behavior of ^{27}K strongly supports that UNi_2Al_3, like UPt_3 and Sr_2RuO_4, belongs to a class of spin-triplet SC pairing state superconductors.

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Heavy-fermion (HF) superconductors have attracted much interest since an intricate relation between magnetism and superconductivity has been reported in these compounds. In this context, respective isostructural hexagonal compounds UPd_2Al_3 and UNi_2Al_3 are of special interest, since antiferromagnetic (AF) long-range order with $T_N = 14.3$ and 4.5 K is found to coexist with the superconductivity with $T_c \sim 2$ and 1 K, respectively [1,2]. In UPd_2Al_3, neutron-diffraction (ND) experiments [3] revealed a commensurate magnetic structure with a large ordered magnetic moment $\mu = 0.85\mu_B$ on the uranium atoms. On the other hand, ND [4] and muon spin rotation (μSR) [5] experiments revealed that UNi_2Al_3 orders in a spin-density wave (SDW) with an incommensurate wave vector $Q_0 = (H \pm 0.61, 0, 0.5)$ and has a tiny magnetic moment of $\sim 0.2\mu_B$ modulated in amplitude within the basal plane.

As for the superconducting (SC) properties, the large values of both specific-heat jump at T_c and the Sommerfeld coefficient of the electronic normal-state specific heat, $\gamma = 140$ and 120 mJ/K^2 mol for UPd_2Al_3 and UNi_2Al_3, respectively, point to the formation of a HF pairing state below T_c. In UPd_2Al_3, the NMR Knight shift decreases below T_c irrespective of the direction of the magnetic field, and the nuclear spin-lattice relaxation rate, $1/T_1$, obeys a T^3 law in the SC state. This behavior is consistent with a spin-singlet d-wave superconductivity with a line-node gap [6,7]. In contrast, the SC nature in UNi_2Al_3 has been studied only by a few experiments owing to the difficulty of preparing a SC single crystal. Dalichaouch *et al.* [8] and Sato *et al.* [9] independently measured the field dependence of the resistive SC transition, and showed that paramagnetic limiting, which is usually seen in the spin-singlet SC state, does not play any role in UNi_2Al_3. This means that the upper critical field $H_{c2}(T)$ is completely dominated by orbital effects, consistent with a hypothesis of spin-triplet superconductivity in UNi_2Al_3. Concerning the SC gap structure in UNi_2Al_3, Tou *et al.* reported from T_1 measurements that the gap vanishes along line nodes as in UPd_2Al_3 [10]. However, Knight shift measurements, which give crucial information about the symmetry of the pairs, have not yet been reported due to the lack of the high-quality single crystal.

In this paper, we report first precise measurement of the ^{27}Al Knight shift (^{27}K) in UNi_2Al_3 that allows us to determine the spin state of the Cooper pairs. The single crystal used here shows a resistive SC transition at $T_c = 0.91$ K with $\Delta T_c \sim 50$ mK [9]. When a static field $\boldsymbol{H}_0$ is applied to the c axis ($\boldsymbol{c}$) ($\theta = 0°$), five sharp peaks in $^{27}Al(I = 5/2)$-NMR spectrum are well split by the nuclear electric quadrupole interaction. Here θ is defined as the angle between $\boldsymbol{H}_0$ and $\boldsymbol{c}$, which is the principal axis of the electric field gradient. The linewidth of the central peak ($1/2 \leftrightarrow -1/2$ transition) is narrow, approximately 7 Oe at $\boldsymbol{H}_0 \sim 11.9$ kOe and $T = 10$ K, ensuring the high quality of the sample on a microscopic level. The point symmetry of Al sites in the hexagonal crystal structure of UNi_2Al_3 is not axially symmetric, so the quadrupole splitting ν_a along a is no longer equal to the quadrupole splitting ν_b along $\boldsymbol{b}$. For $\boldsymbol{H}_0 \parallel \boldsymbol{a}$ ($\boldsymbol{H}_a$) ($\theta = 90°$), there exist two inequivalent Al sites. For one third of the Al sites, $\boldsymbol{H}_0$ is parallel to $\boldsymbol{a}$ (denoted as the $\phi = 0°$ site) and, for two thirds of the Al sites, the angle between $\boldsymbol{H}_0$ and $\boldsymbol{a}$ is $\pm 60°$ (denoted as the $\phi = 60°$ site).

In general, the shift of the central peak in the NMR spectrum is expressed as $K(T) = K_s(T) + K_{orb} + K_Q(H)$. Here K_s and K_{orb} are the spin and orbital components of the Knight shift and only K_s is T dependent. Note that the quadrupolar shift, K_Q, originates from the second order electric quadrupole interaction and is inversely proportional to H^2. In order to deduce K_s, $^{27}K(T)$ was measured under a strong field of $\boldsymbol{H}_0 = 58.5$ kOe so that $K_Q \propto 1/H^2$ can be neglected. For $\boldsymbol{H}_a$, as expected, two peaks corresponding to the $\phi = 0°$ and $\phi = 60°$ Al sites are well resolved as seen in the inset of Fig. 1(a). The T dependence of K^c along the c axis and K at the $\phi = 0°$

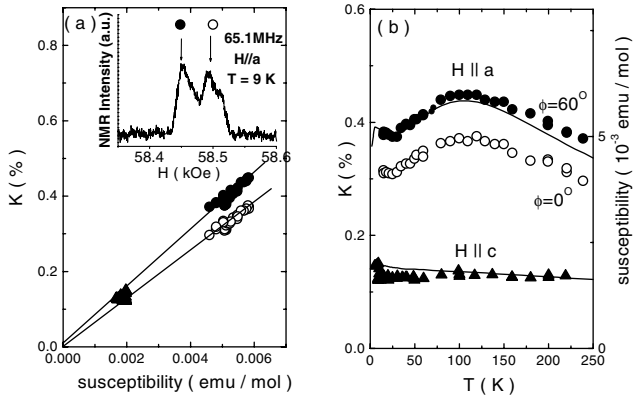

FIG. 1. (a) K-χ plot with T as an implicit parameter. The inset shows the ^{27}Al NMR spectrum for $\boldsymbol{H}_0 \parallel \boldsymbol{a}$. The two peaks correspond to $\phi = 60°$ and $\phi = 0°$. (b) T dependence of ^{27}K at the $\phi = 0°$ and $\phi = 60°$ peaks for $\boldsymbol{H}_0 \parallel \boldsymbol{a}$ and for $\boldsymbol{H}_0 \parallel c$ [$^{27}K^c$ (triangles)] in UNi_2Al_3. Solid curves: bulk susceptibility for the single crystal along $\boldsymbol{a}$ and $\boldsymbol{c}$ axes, respectively [9].

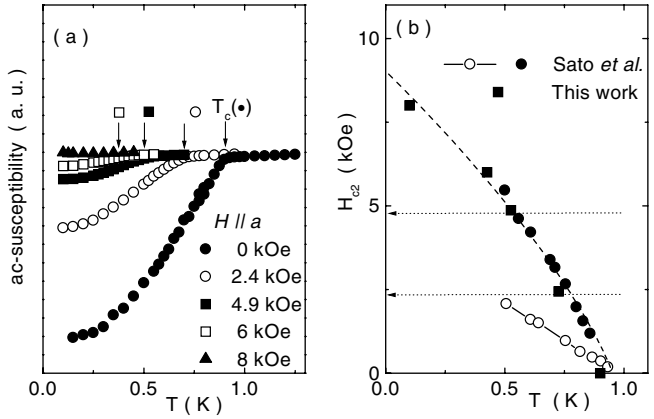

FIG. 2. (a) Variation of χ_{ac} from the NMR coil inductance for various applied fields parallel to $\boldsymbol{a}$. (b) T dependence of the anisotropic upper critical field determined from resistivity measurements [open ($\boldsymbol{H}_0 \parallel \boldsymbol{c}$) and solid ($\boldsymbol{H}_0 \parallel \boldsymbol{a}$) circles] [9]. The present results determined by χ_{ac} for $\boldsymbol{H}_0 \parallel \boldsymbol{a}$ (solid squares) are also plotted. H_{c2} at 100 mK was determined from H dependence of the SC diamagnetism. The dotted arrows indicate the magnetic fields at which the Knight shift was measured.

and 60° sites for $\boldsymbol{H}_0 \parallel \boldsymbol{a}$ is presented in Fig. 1(b). The T dependence of K is in good agreement with that of the bulk susceptibility (χ) indicated by solid curves in Fig. 1(b).

From the $K(T)$ vs $\chi(T)$ plots, the hyperfine coupling constants A_{hf} at $\phi = 0°$ and $\phi = 60°$ sites are estimated to be 3.5 and 4.2 kOe/μ_B, respectively, and K_{orb} at both sites is shown to be negligibly small. It should be noted that K^c exhibiting a weak T dependence, when plotted against χ_c, falls approximately on the linear line fitted to the $K^{\phi=0}(T)$ vs $\chi_a(T)$ plot, indicating that A^c_{hf} is comparable to $A^{\phi=0}_{hf}$. In UNi_2Al_3, $A^{\phi=0}_{hf}$ and $A^{\phi=60}_{hf}$ are close to $A_{hf} = 3.12$ and 3.94 kOe/μ_B found in UPd_2Al_3 [6]. The positive and nearly isotropic hyperfine coupling constants suggest that the Al 2s Fermi-contact contribution is dominant. The spin susceptibility is thus directly related to the measured Knight shift.

The T_c under various $\boldsymbol{H}_a$ was determined by the ac susceptibility measurement using an *in situ* NMR coil as displayed in Fig. 2(a). Figure 2(b) indicates the upper critical field (H_{c2}) obtained by the present experiment, along with the data obtained from the resistivity measurements [9]. The Knight shift was measured at $\boldsymbol{H}_a = 2.43$ and 4.89 kOe as marked by the dotted arrows in Fig. 2(b).

The inset of Fig. 3(a) shows the ^{27}Al-NMR spectrum at $T = 102$ mK and $\boldsymbol{H}_a = 2428$ Oe, which is decomposed into the two spectra at $\phi = 0°$ and 60° Al sites as indicated by dashed lines. Using the electric quadrupole frequency, $\nu_Q = 0.777$ (MHz) and asymmetry parameter, $\eta \equiv (\nu_x - \nu_y)/\nu_z = 0.323$, $K_Q^{\phi=0}(H)$ and $K_Q^{\phi=60}(H)$ are estimated to be 4.68% and 3.44%, respectively, at $\boldsymbol{H}_a = 2428$ Oe. Therefore, the NMR experiment on a single crystal enables us to measure K at the $\phi = 60°$ site precisely. It is obvious that the peak corresponding to the $\phi = 60°$ site does not shift at all down to $T = 49$ mK across T_c, as seen in Fig. 3(a). As temperature is cooling down across $T_c(H) \sim 0.75$ K that was determined by the ac-susceptibility and T_1 measurements as indicated in Figs. 4(a) and 4(b), the $K_s^{\phi=60}(T)$ does not change as seen in Fig. 4(c). The same result was also obtained for $\boldsymbol{H}_a = 4887$ Oe. At this field, the NMR lines at the $\phi = 0°$ and 60° sites are not well resolved, but overlap because of comparable values of $K_Q(H)$ as indicated in the inset of Fig. 3(b). It should, however, be noted that the broad NMR spectrum does not exhibit any shift down to 50 mK across $T_c(H) \sim 0.50$ K as seen in Fig. 3(b). This invariance of the shift for $\boldsymbol{H}_a = 2438$ and 4887 Oe reveals that the Knight shift, and therefore the spin susceptibility, does not change at all on passing through $T_c(H)$.

Next we compare the ^{27}Al shift results in UNi_2Al_3 with those in the isostructural compound UPd_2Al_3.

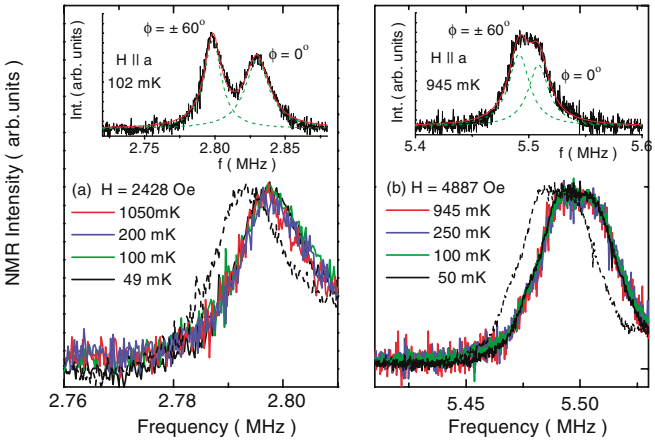

FIG. 3 (color). The peak of ^{27}Al NMR spectra corresponding to the $\phi = 60°$ site taken at various T for $\boldsymbol{a} \parallel \boldsymbol{H}_0 = 2428$ Oe (a) and 4887 Oe (b), respectively. The NMR-spectrum peak shown by the dotted line in two figures is the lowest-T peak shifted to 0.15% that is the Knight shift decrease seen in UPd_2Al_3. The inset of the two figures shows decomposition of the central peak by two $\phi = 60°$ and $\phi = 0°$ peaks.

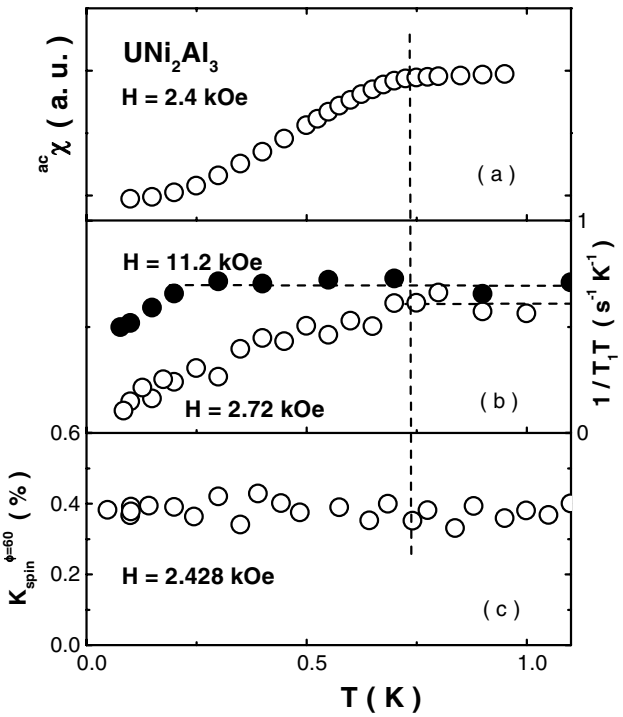

FIG. 4. T dependence of (a) ac susceptibility, (b) $1/T_1T$ for $\boldsymbol{a} \parallel \boldsymbol{H}_0 = 2.72$ kOe (open circles), and 11.2 kOe (solid circles) [23], and (c) Knight shift at the $\phi = 60°$ peak. The vertical dotted line indicates T_c (2.4 kOe).

The shift associated with itinerant heavy electrons in UPd_2Al_3 exhibits a distinct decrease $\Delta K_{ab} \sim -0.15\%$, and $\Delta K_c \sim -0.10\%$ in the SC state [6,11,12]. The large residual Knight shift that remains even at the lowest T was ascribed to the localized part of $5f$ electrons that order antiferromagnetically with an atomiclike value of the saturation moment, $\mu \sim 0.85\mu_B$. The ΔK in UPd_2Al_3 reveals that the spin susceptibility of the heavy itinerant electrons diminishes in the SC state due to the formation of spin-singlet Cooper pairs. The value of the Knight shift for these electrons was estimated to be $K_s \sim 0.14\%$ using $\gamma = 150$ mJ/mol K^2 just above T_c and $A_{hf} \sim 3.5$ kOe/μ_B [13]. Here the Fermi liquid relation $\chi = \gamma$, in units of $\hbar = \mu_B = k_B = 1$, and the relation $K = A_{hf}\chi/N\mu_B$ between the shift and the susceptibility are used. If the same calculation is applied to UNi_2Al_3, $K_s \sim 0.16\%$ is calculated, using $\gamma = 140$ mJ/mol K^2 just above T_c [9,14] and $A_{hf}^{\phi=60} = 4.2$ kOe/μ_B. This suggests that if spin-singlet superconductivity were realized in UNi_2Al_3, ^{27}K in proportion to K_s should diminish as much as in UPd_2Al_3. The value of 0.15% that is the Knight shift decrease in UPd_2Al_3 is apparently greater than the experimental error ($\leq$1 kHz) and is large enough to be resolved from the present measurements as indicated in Figs. 3(a) and 3(b). To demonstrate this, the lowest-T spectrum that is shifted as much as 0.15% is indicated by a dotted line in both figures. The present results indicate clearly invariance of NMR spectra on passing through $T_c(H)$. One might, however, suspect that the Knight shift does not decrease in UNi_2Al_3 due to an impurity induced spin-orbit scattering [15]. It should be noted that the residual resistivity in single-crystal UNi_2Al_3 ($\rho_0 \sim 3.6\ \mu\Omega$ cm) is small with a comparable value to that in UPd_2Al_3 ($\rho_0 \sim 3.3\ \mu\Omega$ cm) [16], indicative of the high quality of both samples. The contrasting behavior of ^{27}K below T_c in UPd_2Al_3 and UNi_2Al_3 is, therefore, not ascribed to an impurity effect or crystal imperfections. Rather, the invariance of ^{27}K against the onset of superconductivity suggests strongly that a spin-triplet pairing state is realized in UNi_2Al_3, with parallel spin pairing in the ab plane. In order to examine the detailed nature of the triplet SC order parameter, a K^c measurement is needed. However, the width of the NMR spectrum along the c axis is significantly larger than in the ab plane because the internal field due to the SDW ordering arises dominantly along the c axis [6,10], preventing a precise K^c measurement in the SC state.

We speculate that the contrasting SC nature of these isostructural compounds is related to the difference in magnetic characters in the magnetically ordered state. The relaxation rate $^{27}(1/T_1)$ in UPd_2Al_3 shows a gaplike decrease below the onset of magnetic order and is not dominated by spin excitations associated with localized moments. The behavior of $T_1T =$ const, which was observed above T_c [6], points to the persistence of the HF state well below T_N, consistent with the observation of the larger γ value of 150 mJ/mole K^2. In the SC state, ND experiments revealed a double-peak structure in the inelastic ND spectrum below T_c. The lower-energy peak was identified as a mode associated with the itinerant HF's, whereas the higher peak is associated with a gapped spin-wave mode in the magnetically ordered state [17–19]. These experimental results suggest that the localized and itinerant characters of the $5f$ electrons are well separated in the SC state of UPd_2Al_3 as discussed above. Quite recently, Sato *et al.* suggested from these experimental results that a "magnetic exciton," which is a local crystal-field excitation by the exchange interactions between localized moments, is mediating superconductivity in UPd_2Al_3 [20]. In contrast, the T dependence of $1/T_1$ in UNi_2Al_3 was found consistent with the itinerant SDW type [6]. Correspondingly, the ND experiments found no double-peak structure in UNi_2Al_3 [14]. The $5f$ electrons in UNi_2Al_3 possess an itinerant character and are in an antiferromagnetic spin-fluctuation regime in the paramagnetic state as evidenced by the T_1 measurement. In this sense, the magnetic-exciton scenario proposed for UPd_2Al_3 cannot be applied to UNi_2Al_3, and superconductivity in UNi_2Al_3 must be addressed on an itinerant electron model. Thus, it is likely that the difference in their SC nature might be ascribed to the different characteristics of the magnetically ordered state.

Finally, in order to gain an insight into the possible origin of spin-triplet superconductivity in UNi_2Al_3, we comment on the character of spin fluctuations both in the paramagnetic and in the ordered states. The inset of Fig. 5

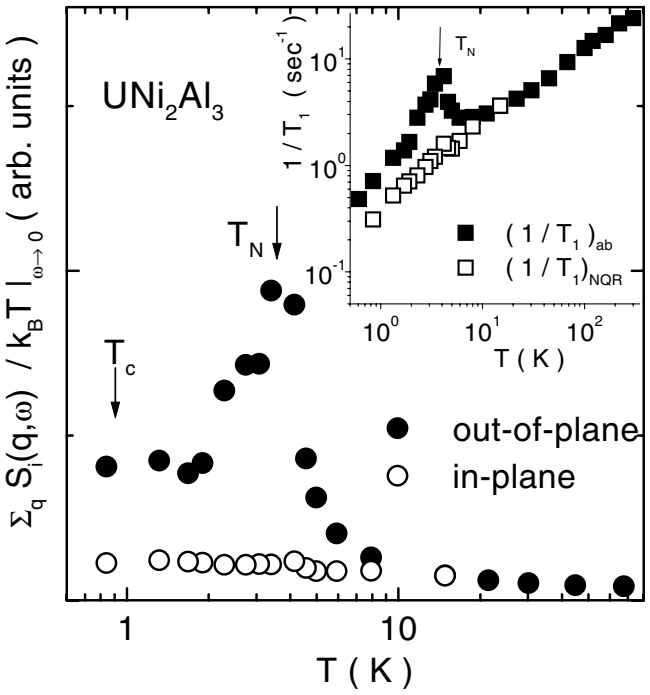

FIG. 5. T dependence of the out-of-plane and in-plane components of the q-summed dynamic structure factor $\sum_q S(q,\omega)$ normalized by k_BT. Inset: T dependence of $1/T_1$ by NQR $[(1/T_1)_{\rm NQR}]$ and NMR with $\boldsymbol{H}_0 \perp \boldsymbol{c}$ $[(1/T_1)_{ab}]$ (see text).

shows the T dependence of $1/T_1$ for the polycrystalline sample [13]. Relaxation measurements were carried out using nuclear quadrupole resonance (NQR), and NMR with the magnetic field parallel to the ab plane. In general, $1/T_1$ probes the q summation of the transverse component of the dynamical structure factor $S(q,\omega)$ with respect to the quantization axis at the low energy ω_n equivalent to the NMR or NQR frequency. Specifically, $(1/T_1)_{\rm NQR}$ and $(1/T_1)_{ab}$ are related to the in-plane (in) and out-of-plane (out) components of $S_i(q,\omega)$ as follows: $^{27}(1/T_1)_{\rm NQR} \propto \sum_q [2|^{27}A_{\rm hf}^{ab}|^2 S_{\rm in}(q,\omega_n)]$ and $^{27}(1/T_1)_{ab} \propto \sum_q [|^{27}A_{\rm hf}^{c}|^2 S_{\rm out}(q,\omega_n) + |^{27}A_{\rm hf}^{ab}|^2 S_{\rm in}(q,\omega_n)]$. Using the relations and the isotropic $^{27}A_{\rm hf}$ as shown above, $\sum_q S_{\rm out}(q,\omega_n)$ and $\sum_q S_{\rm in}(q,\omega_n)$ normalized by k_BT can be calculated and are shown in the main part of Fig. 5. The anisotropy in $\sum_q S(q,\omega_n)$ becomes apparent below 10 K. Its out-of plane component exhibits a large enhancement at $T_{\rm N}$ due to critical spin fluctuations towards the SDW transition, whereas the in-plane component remains nearly unchanged upon cooling below $T_{\rm N}$. Even for $T \sim T_c$, the ratio $\sum_q S_{\rm out}(q,\omega_n)/\sum_q S_{\rm in}(q,\omega_n) \sim 4$ remains large. This means that the magnetic excitations in the SDW state are anisotropic, presumably due to the spin-orbit interaction.

Quite recently, Kuwabara and Ogata have proposed that anisotropic incommensurate AF spin fluctuations associated with a nesting property of the Fermi surfaces stabilize spin-triplet superconductivity in Sr_2RuO_4 [21]: When the out-of-plane component of spin fluctuations is larger than the in-plane one and, at the same time, the system is quite close to the AF instability, spin-triplet superconductivity occurs with parallel spin pairing in the ab plane [22]. We point out that this scenario may be applicable to UNi_2Al_3 because the magnetic excitations remain anisotropic even in the SDW state.

In conclusion, we have reported ^{27}K, $1/T_1$, ac-susceptibility measurements on a high-quality single crystal of UNi_2Al_3 that exhibits a sharp SC transition at $T_c \sim 0.9$ K. The spin part of ^{27}K that was deduced to be $K_{\rm s} \sim 0.35\%$ along the a axis remained unchanged across $T_c(H)$. The present result gives strong evidence for spin-triplet superconductivity in UNi_2Al_3. This is in contrast to the isostructural HF superconductor UPd_2Al_3 that exhibits singlet d-wave superconductivity.

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