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Orbital ordering in the half-Heusler-type compound UPtSn: Evidence from ^{119}Sn and ^{195}Pt NMR studies

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We present the results of combined macroscopic [x-ray diffraction (XRD)] and microscopic [nuclear magnetic resonance (NMR)] studies on cubic UPtSn. From the ^{119}Sn and ^{195}Pt NMR spectra the occurrence of the phase transition suggested by the specific heat anomaly at $T_0=35$ K has been confirmed. The observation of anisotropic line shapes of both ^{119}Sn and ^{195}Pt resonances provides direct microscopic evidence for the symmetry lowering below T_0, although no lattice distortion was observed in the XRD experiment. Such a behavior is attributed to the occurrence of long-range uranium $5f$-orbital ordering.

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The specific heat data obtained on the half-Heusler-type compound UPtSn, crystallizing in a cubic MgAgAs-type of structure (space group $F\bar{4}3m$) revealed pronounced λ-like anomaly at $T_0=35$ K, suggesting some sort of phase transition.[1,2] This phase transition is peculiar and the order parameter has not been established up to now. At first, this transition was expected to have a magnetic origin[2] similar to that of the isoelectronic and isostructural type-I antiferromagnet UNiSn ($T_N=43$ K) (Ref. 3). Theoretical calculations[4,5] predict an antiferromagnetic (AFM) ordering in UPtSn. However, no magnetic reflection has been observed in neutron diffraction experiments [R. Troć and G. André (unpublished)]. The nuclear magnetic resonance (NMR) technique is sensitive to a change of magnetic state through hyperfine (HF) interactions. Usually, antiferromagnetic ordering (if present) is signalized by an abrupt change in the Knight shift or linewidth due to the presence of a static internal magnetic field. And so, in UNiSn the NMR signal of ^{119}Sn nuclei even disappears below T_N due to the presence of large static internal magnetic fields at the Sn sites.[6] The NMR is also a very sensitive tool in detecting the low temperature phase transitions (with or without Jahn-Teller lattice distortions) driven by the ordering of multipolar (quadrupolar or octupolar) moments.[7] In UNiSn the AFM ordering is accompanied by a tetragonal distortion ($|1-c/a| \leqslant 3\times10^{-3}$) of the crystallographic unit cell below T_N driven by ferroquadrupolar ordering.[8,9] An important question in UPtSn is whether there is a structural distortion at T_0 either external (i.e., a reduction in the total symmetry; e.g., from cubic to tetragonal) or internal (i.e., atomic displacement from regular crystallographic positions). The first reference to an x-ray experiment designed to determine the unit-cell dimensions of UPtSn at low temperature appears in Ref. 2. No deviation from cubic symmetry was found below T_0 but a precision of the experiment was not defined.

The aim of the present work was to use the ^{119}Sn and ^{195}Pt NMR for investigation of microscopic properties of UPtSn. To our knowledge no such data have yet been reported. In this paper, we only deal with a narrow temperature range around T_0, where we focus our attention on external crystal symmetry and the symmetry properties of the Knight shift tensors at Sn and Pt sites.

A polycrystalline sample of UPtSn was prepared by melting the pure elements in an arc furnace and annealing the obtained ingot under vacuum at 850 °C for one week. The x-ray studies were carried out on Siemens D5000 powder diffractometer using Ni-filtered Cu $K\alpha$ radiation both at 300 and 16 K. The low temperature measurements were performed using continuous ^{4}He flow cryostat (Paar). The x-ray diffraction (XRD) patterns with narrow Bragg peaks indicate that the UPtSn sample is a single phase and retains the cubic MgAgAs-type structure in the whole temperature range investigated.

The ^{119}Sn $(I=\frac{1}{2})$ and ^{195}Pt $(I=\frac{1}{2})$ NMR measurements were performed in the temperature range 20–300 K using a Bruker Avance DSX-300 spectrometer operating at a field $B_0=7.05$ T and temperature controller ITC-503 (Oxford Instruments Co Ltd.). A two pulse sequence $(90^\circ_x-\tau-90^\circ_y)$, frequently used for materials exhibiting inhomogeneously broadened resonance lines,[10] was applied in order to excite a nuclear spin echo. Quadrature detection and phase cycling procedures were used for removal of baseline artifacts from the spin-echo data.[11] The second half of the spin echo was Fourier transformed and different spectra for different frequency settings were overlayed (frequency-sweep spectra).[12] The ^{119}Sn and ^{195}Pt Knight shifts (K) are given with reference to $\Xi\,^{119}\mathrm{Sn}=0.372\,906\,32$ and $\Xi\,^{195}\mathrm{Pt}=0.214\,000\,00$, respectively. Here Ξ is defined as the ratio of the isotope-specific frequency to that of ^1H in tetramethylsilane in the same magnetic field (IUPAC δ scale).

We were particularly careful to explore the region near 35 K to search for signatures of the phase transition indicated by the specific heat experiment. Figures 1 and 2 show the temperature dependencies of the ^{119}Sn and ^{195}Pt NMR frequency-sweep spectra obtained at a resonant magnetic field of 7.05 T. For $T>35$ K, single-site, narrow, and symmetric spectra have been obtained. This indicates that there is no anisotropic NMR shift at both Sn and Pt sites, reflecting their tetrahedral point symmetry above T_0. On the other hand, the spectra recorded at $T\leqslant35$ K reveal the powder-pattern line shapes characteristic for a situation when a nucleus under investigation (^{119}Sn or ^{195}Pt) is in an environment of axial symmetry. In such a case the hyperfine interaction produces a NMR Knight shift, $K(\Theta)$

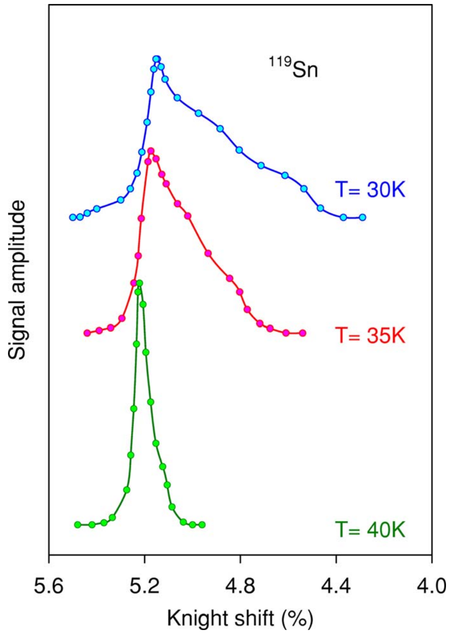

FIG. 1. (Color online) Evolution around T_0 of the frequency-sweep ^{119}Sn NMR spectra in UPtSn. For better presentation the amplitude of the spectrum at 40 K has been reduced by factor of 2.

$=K_{iso}+K_{an}(3\cos^2\Theta-1)$, where K_{iso} and K_{an} are the isotropic and anisotropic components of the Knight shift, respectively, and Θ is the angle between the local symmetry axis and the applied magnetic field B_0. Then, the powder pattern shows a peak at $K_\perp=K_{iso}-K_{an}$ and a shoulder at $K_\parallel=K_{iso}+2K_{an}$, so that the width is given by $\Delta=K_\parallel-K_\perp=3K_{an}$. Here $K_\parallel$ and $K_\perp$ represent the Knight shifts parallel and perpendicular to the symmetry axis, respectively.[13] It is remarkable that $K_{iso}>0$ and $K_{an}<0$ for the Sn sites, while $K_{iso}<0$ and $K_{an}>0$ for the Pt site. In the paramagnetic state, well above T_0, we have found that $\partial K/\partial\chi$ is positive for Sn nuclei and negative for Pt nuclei with $|H_{hf}(Sn)/H_{hf}(Pt)|\approx 4$, where χ represents the bulk magnetic susceptibility and H_{hf} are respective transferred hyperfine coupling constants (detailed results will be published elsewhere). The large and positive ^{119}Sn K_{iso} is due to the polarization of conduction s electrons by $5f$ electrons, while the negative ^{195}Pt K_{iso} suggests an important role of the core-polarization process in the hyperfine interaction. At ambient temperature, UPtSn crystallizes in the MgAgAs-type of structure with the cubic space group $F\bar{4}3m$, where all elements of UPtSn have the same site symmetry $\bar{4}3m$. Therefore, the observation of anisotropic line shapes of both ^{119}Sn and ^{195}Pt resonance provides microscopic evidence for the symmetry lowering below T_0 in UPtSn.

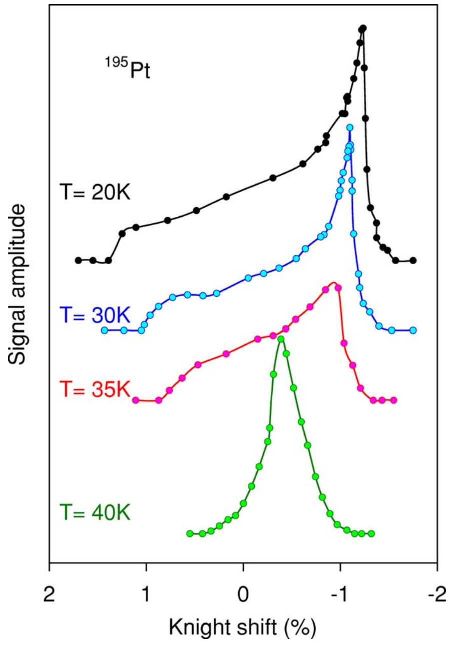

FIG. 2. (Color online) Evolution around T_0 of the frequency-sweep ^{195}Pt NMR spectra in UPtSn.

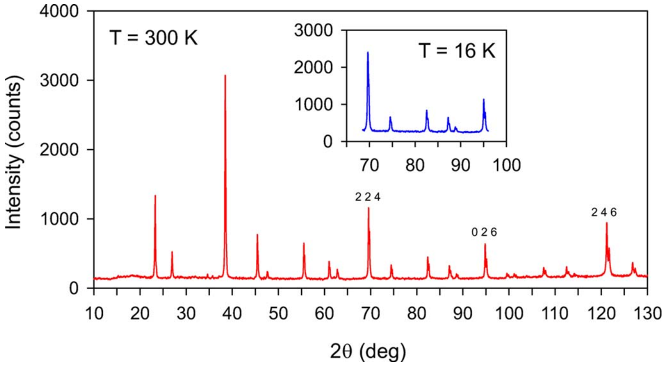

FIG. 3. (Color online) X-ray powder diffraction diagrams of UPtSn recorded at 300 and 16 K. Miller indices of three reflections chosen for precise scans are shown.

To verify it we have monitored the position and shape of all reflections in the x-ray diffraction patterns recorded above and below T_0. In particular, anticipated tetragonal distortion of the unit cell in the low temperature phase would result in a splitting of the 224 Bragg reflection into doublet, and splitting of 026 and 246 reflections into triplets (or at least a broadening of their widths). Inspection of Figs. 3 and 4 clearly shows absence of any change in the shape and width of investigated reflections. We note here that double peak structure of each reflection both in high and low temperature phases is due to the existence of the Cu $K\alpha_{1,2}$ doublet. The shift of the whole spectrum to higher values of the diffraction angles, 2θ, is due to a thermal contraction of the lattice in a low temperature phase. Our x-ray diffraction results show to high accuracy that no measurable external deviation from the cubic structure occurs below T_0, so that the anisotropy of NMR spectra from this source is effectively ruled out.

We believe the symmetry lowering without lattice distortion to be a clear observation of orbital ordering (ordering of U-$5f$ quadrupoles) through the symmetry breaking of the HF coupling. Both the ^{119}Sn and ^{195}Pt NMR spectra below T_0 gradually broaden with decreasing temperature. The effect seems to be magnetic in origin. However, the full widths ($\triangle$) indicate the absence of any large internal fields at and below T_0. At $T=35$ K, $\Delta\approx 0.03$ T at the Sn sites and $\Delta\approx 0.11$ T at the Pt sites. It was recently shown[7] that weak AFM moments can be field-induced in the systems exhibiting quadrupolar

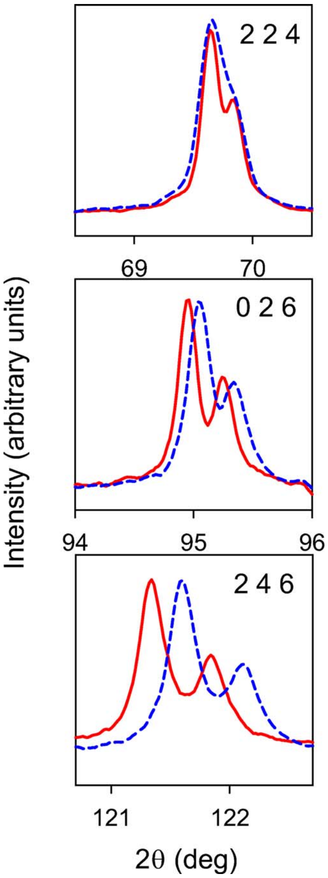

FIG. 4. (Color online) Comparison of the profiles of three chosen reflections at 300 K (solid line) and 16 K (dashed line). Profiles are rescaled to the common intensity, each contains both $K\alpha_1$ and $K\alpha_2$ component of the Cu radiation.

order. These AFM moments produce a static HF coupling at the interstitial ligand atom sites.

In some aspects UPtSn resembles NpO_2 crystallizing in the cubic CaF_2-type of structure, where the phase transition at $T_0=25$ K is purely electronic (usual magnetic dipole ordering is excluded) and does not involve either internal or external crystallographic distortions. It was suggested[14,15] that the resonant x-ray scattering experiments can be explained by assuming the electric longitudinal triple-**q** antiferroquadrupole order induced from the primary longitudinal triple-**q** antiferrooctupole order. As a consequence of the quadrupolar order, the symmetry is lowered from $Fm\bar{3}m$ to $Pn\bar{3}m$, in which oxygen ions can occupy two inequivalent positions (cubic and tetragonal) in a ratio 1:3. Quite recently, from the ^{17}O NMR spectra, the occurrence of two inequivalent oxygen sites below T_0 in NpO_2 has been confirmed[16] strongly supporting an idea of the longitudinal triple-**q** multipole structure in NpO_2.

A good example of the internal distortion accompanying the first-order transition to the AFM state is UO_2, where the displacement of the oxygen atoms from the fluorite lattice positions does not require a corresponding change in the unit-cell dimensions.[17] Here, contrary to the case of UNiSn, the NMR signal does not disappear below T_N and the internal lattice distortion is monitored by oscillatory ^{17}O spin-echo modulation.[18] The symmetry is lowered from $Fm\bar{3}m$ to $Pa\bar{3}$ as a consequence of a transverse triple-**q** AFM structure in which all oxygen sites occupy equivalent position and single-site spectra are observed.

Such scenarios are not excluded in UPtSn. We cannot, however, directly prove the multipolar model from the NMR data alone. Further experimental and theoretical investigations are necessary. We note that even the ground state of the crystalline electric field level scheme is not yet established. An absence of any crystallographic distortion and lack of conventional dipole magnetic order below T_0 as reported in Ref. 2 need independent verification. New x-ray and neutron diffraction measurements and ^{119}Sn Mössbauer experiments are planned.

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