The Nuclear Magnetic Resonance of ^{235}U in Condensed Matter Research

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This spring the uranium NMR Group at JAERI has come together for the first time. In this brief article we would like to give a down-to-earth view of what our goals are, why we think they are interesting, and how we propose to go about achieving them.

Shortly after the discovery of nuclear magnetic resonance in 1946, Walter Knight reported an NMR frequency shift occurring in copper metal,[1] and the field of solid state NMR was born. There followed a period of rapid development where the most widely used tools of this trade...spin echoes[2], spin-lattice relaxation and the Korringa relation,[3] indirect RKKY spin-spin coupling,[4] and nuclear quadrupole resonance (NQR),[5] to name a few...were put in place. These methods rapidly became the elements of a powerful investigative tool, and has for many years been a standard technique to characterize static and dynamic magnetism in systems of interest. There have been many occasions where NMR studies have played a major role in the unfolding of high-profile condensed matter physics. Superconductivity is a good example, where the now famous density-of-states peak driving the sub-T_c spin-lattice relaxation rate[6] helped to verify the Nobel Prize-winning BCS theory. NMR studies of (the absence of) this effect in the high-T_c compounds, as well as many other phenomena of interest, constitute an equally prominent recently-written chapter in the NMR story.

In the past decade or so, the field of actinide research has come to considerable prominence, because of the current fashionability of correlation effects in interacting fermion systems. The correlated motion of the 5f electrons in intermetallic compounds leads to a number of exotic behaviors for which a satisfactory understanding has yet to be achieved. We give here a short list of effects, mentioning a few uranium compounds as examples: "Magnetic" ordering with anomalously small ordered moments (URu_2Si_2, UPt_3); magnetic ordering and superconductivity coexisting in the same system (UPd_2Al_3, UNi_2Al_3, UGe_2); P-wave or other exotic superconducting order parameters (UPt_3, UBe_{13}); and quantum critical point behavior (UPt_2In, UNiAl, UGe_2, and UPd_2Ga_3). While numerous NMR studies of ligand nuclei have been reported for these systems, for each there exists a strong possibility of contrasting fermion behavior as seen at the ligands as compared with that found at uranium sites. The ideal probe for uranium site behaviors would be the ^{235}U NMR itself, but up to now no such study has been reported. The Uranium NMR Group is proposing to undertake ground-breaking ^{235}U NMR studies in these systems.

To step back for a moment, it was only recently

that the ^{235}U NMR of a solid phase compound (UO_2) was reported for the first time[7] by the A.S.R.C. director, Dr. H. Yasuoka and his student Dr. K. Ikushima, who is currently a member of our group. The reason for this is that ^{235}U in solids is without doubt a difficult nucleus to observe using resonance techniques. Because of its tiny magnetic moment, extremely large quadrupolar energies, and low abundance, ^{235}U NMR lines are typically broad and weak. Furthermore, unusually strong hyperfine couplings with 5f electron magnetic moments, typical of the actinides in general, often render the spin-lattice relaxation times unmanageably short. Add to this the special procedures required to deal safely with the radioactivity of an enriched ^{235}U specimen, and one may not be surprised that this particular nuclear species has lain dormant for many decades. There is for our research group a serious question of how to overcome these difficulties in pursuing our objective, which is to measure ^{235}U NMR parameters.

We consider briefly the strategies available to us in pursuit of the goals described above. As was implied earlier, it is not always feasible to detect the ^{235}U NMR directly. There is, however, an entire family of indirect methods for measuring the ^{235}U NMR parameters such as frequency shift and relaxation time, where one does not observe the ^{235}U NMR directly. While such techniques may not always be comprehensive in scope, i.e., may be limited to certain systems or ranges of temperature, we anticipate that a wealth of interesting and useful data may nonetheless be obtained. We give here two examples of indirect methods.

The most basic indirect method of observation is simple cross relaxation as illustrated in Fig.1. There, neighboring nuclear spins are depicted by the large red (ligand) and small blue (^{235}U) arrows. Via dipolar or indirect spin-spin coupling, the ^{235}U produces a small ($\sim$ 0.1 $\rightarrow$ 1.0 Gauss) local field (green arrow) at the ligand neighbor. Spin-lattice relaxation causes the uranium spin to fluctuate up and down as shown. This produces a dynamic cross-relaxation effect for the ligand spin echo (see Fig.2a). Over temperatures where the ^{235}U fluctuation rate (i.e., T_{1U}) has a suitable range of values, estimates of the worst-case scenario (dipolar coupling only) suggest that this relaxation effect is easily measurable. A comprehensive study of the cross relaxation effect is expected to yield the magnitude and temperature dependence of T_{1U}. This method is relatively easy to implement, but does not yield spectroscopic data.

Another method, the technique of spin echo double resonance, is illustrated in Fig.2. This technique does involve irradiation of the ^{235}U resonance line(s), and can therefore be a sensitive probe of the NMR frequency shift. The ligand NMR is presumed to offer an easily measured nuclear spin echo signal (Fig.2a). As shown in Fig.2b we now apply a " π -pulse" at the ^{235}U NMR frequency. This has the effect of inverting the local field h_{LU} at the ligand nuclei (as shown in Fig.1), which in turn degrades the echo signal as indicated by the black tracing. By scanning the frequency of the ^{235}U π -pulse in the vicinity of the NMR frequency, it is possible to trace out the uranium line profile as shown in Fig.2c. There are certain conditions which must be met for this method to be workable, mainly that the uranium spins must be static on the time scale of the experiment and that the uranium NMR line must be narrow enough so that a reasonable fraction of the spins can be inverted with a single pulse.

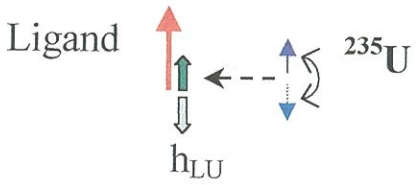

Fig.1. The ^{235}U spin (blue) produces a field hLU at its neighboring ligand nucleus (red). As the ^{235}U fluctuates, the corresponding field fluctuations generate a relaxation process for the ligand spin echo.

For compounds which are not suited to the SEDOR technique, there is a family of double resonance methods which come under the heading of "rotating frame methods" and are somewhat more elaborate-and more powerful- than the ones described above.[8] Our main point here is that there are alternative means to measure the uranium NMR parameters if direct observation becomes unworkable.

In the course of performing indirect ^{235}U measurements, we shall also investigate the ligand NMR parameters, and here we may draw upon the recent literature as well. The combination of ligand plus ^{235}U results will give a unique and comprehensive picture of microscopic behavior in systems of interest. But most of all, the direct uranium probe will offer an unprecedented glimpse of 5f electron behavior.

Some new development of apparatus will be needed to reach the goals we have in mind. Double resonance studies require only modest additions to the standard NMR spectrometer. Other capabilities we will put in place are experimental measurements at high pressures and at dilution refrigerator temperatures. High pressure effects are interesting for uranium intermetallics because of their typically large Gruneisen constant. For example, the quantum critical points can usually be "tuned" by pressure. We also need to include AC susceptibility measurements at high pressures in order to screen such effects before doing NMR studies. Further, we also need dilution refrigerator temperatures, because for many of the compounds the interesting physics occurs below 1K.

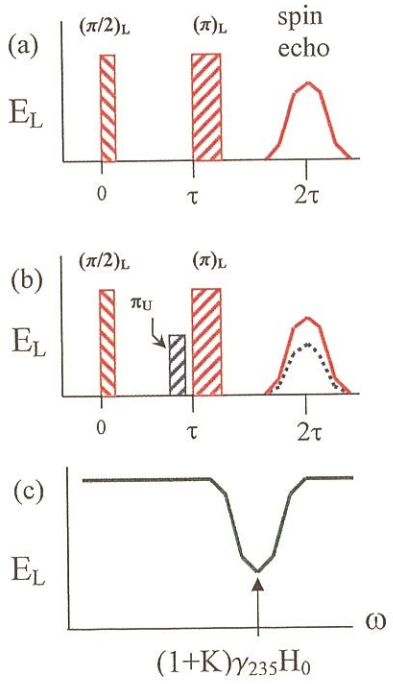

Fig.2. A sequence of cartoons, showing (a) the ligand spin echo, (b) spin echo double resonance (SEDOR), and (c) SEDOR spectroscopy of the uranium line. K is the ^{235}U NMR shift parameter.

In sum, we feel that there is an opportunity here for some pioneering work on an interesting series of compounds. As far as we are aware, no other group here or abroad is undertaking ^{235}U NMR studies. Finally, we would like to emphasize that the JAERI research laboratories, with facilities for handling radioisotopes and with the presence of many groups with similar interests, offers a nearly ideal setting for this research program.

References.

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