^{29}Si NMR and Hidden Order in URu_2Si_2

O. O. Bernal, C. Rodrigues, and A. Martinez
Department of Physics and Astronomy, California State University, Los Angeles, California 90032

H. G. Lukefahr
Department of Physics, Whittier College, Whittier, California 90608

D. E. MacLaughlin
Department of Physics, University of California, Riverside, California 92521

A. A. Menovsky and J. A. Mydosh
Kamerlingh Onnes Laboratory, Leiden University, The Netherlands
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Below $T_N \sim 17$ K the ^{29}Si NMR line in URu_2Si_2 exhibits a previously unobserved field-independent nearly isotropic contribution to the linewidth, which increases to $\sim$12 G as $T \to 0$. We argue that this feature does not arise from static freezing of the U-spin magnetization, but is due to coupling between ^{29}Si spins and a hidden order parameter. We discuss time-reversal symmetry-breaking orbital antiferromagnetism and indirect nuclear spin-spin interactions as possible coupling mechanisms. Further NMR experiments and theoretical calculations are suggested.

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URu_2Si_2 possesses an unusual coexistence of "small-moment" antiferromagnetic (AF) order ($T_N \sim 17$ K) and unconventional superconductivity ($T_c \sim 1.2$ K) [1]. Understanding the magnetic and superconducting behavior of this material has proven to be very challenging and has generated a substantial amount of work over the years (see, e.g., Refs. [1–15], and references therein). The transition at T_N is still puzzling. Although neutron diffraction (ND) experiments indicate AF order [1,2], the ordered-moment size is too small to account for macroscopic effects in the thermodynamic quantities [3]. Thus, many studies have appeared with the goal of elucidating the nature of the true order parameter for this transition. Quadrupolar order has been suggested [4]; some experiments seem consistent with this picture [5], while others are less telling [6]. Experiments also indicate two distinct energy scales in the system [4], corresponding to primary and secondary order parameters. A coupling or switching between the two parameters is also apparent from phenomenological arguments (see Refs. [7] and [8] for recent discussions). In all, several theories involving exotic microscopic mechanisms have been formulated and are still a matter of controversy and debate [9,10].

Recent ND [10] and NMR [11] experiments in URu_2Si_2 under pressure find phase-separated inhomogeneous antiferromagnetism (IAF) with pressure-dependent AF and paramagnetic volume fractions. The moment in the AF phase remains constant at $\sim 0.25\mu_B$/U ion, and the AF fraction decreases with decreasing pressure P to a very small value ($\lesssim 1\%$) at $P = 0$. To date NMR experiments at ambient pressure [11–13] have not observed the line splitting expected from the AF phase, although Luke *et al.* [14] reported a muon spin rotation (μSR) signal from the AF phase which we discuss in more detail below.

The small ambient-pressure AF volume fraction suggests that bulk NMR might not shed much light on the phase transition. However, since NMR can sample electronic effects both directly and indirectly, the absence of line splitting actually offers a chance to characterize more completely the ambient pressure transition at low fields, which continues to be puzzling (i.e., the small AF fraction cannot account for the large thermodynamic and transport effects at T_N). Of particular interest is the possibility of elucidating "hidden order" behavior of the majority paramagnetic fraction of the sample, due to either a time-reversal symmetry-breaking transition or to strong coupling between a charge-order parameter and spin degrees of freedom. Either of these effects should, in principle, be detectable using a spin-1/2 probe like ^{29}Si.

In this Letter we report a new ^{29}Si NMR study at ambient pressure and low magnetic field strengths (below 6 T). We find an unambiguous, field-independent nearly isotropic component λ of the ^{29}Si linewidth which increases below T_N to about 12 G at 4.2 K [15]. This component is static and measures a distribution of local effective fields at the ^{29}Si sites. Its temperature dependence is that of a mean-field order parameter. We argue that λ is unrelated to the static magnetization of the sample and that, instead, it is due to coupling between the ^{29}Si nuclei and the "hidden order" [7] in this system. We discuss the possibility that the effect is due to orbital antiferromagnetism, which implies a time-reversal symmetry-breaking order parameter, as suggested very recently by Chandra, Coleman, and Mydosh [16]. We

also consider a coupling mechanism in terms of indirect interactions between unlike nuclear species. Further NMR experiments and theoretical calculations are suggested to characterize the coupling.

The sample used was a fine powder (particle size $\lesssim 50$ μm) embedded in Stycast 1266 epoxy and oriented in a field of 9.4 T. Alignment of order 90%–95% was estimated for the c axis orientation by comparing the magnetic susceptibility for both transverse ($\mathbf{H} \perp \mathbf{c}$) and longitudinal ($\mathbf{H} \parallel \mathbf{c}$) external fields with that of a single crystal under similar conditions. The alignment method leaves a random distribution of (a, b) basal-plane orientations (tetragonal structure). The ^{29}Si spectral parameters were measured as functions of temperature and applied field for different field directions with respect to the c axis.

Spectra for $\mathbf{H} \perp \mathbf{c}$ and $\mathbf{H} \parallel \mathbf{c}$ [Figs. 1(a) and 1(b), respectively] consisted of a single narrow line [variable-size shoulders ($\sim$0%–15% area) sometimes appear in the spectral tails—see Fig. 1(d) in Ref. [12] for an example]. We fit each line to a Lorentzian function of half width at half maximum (HWHM) $\Gamma(\mathbf{H}, T)$, which we find can be written as $\Gamma^2(\mathbf{H}, T) = \Gamma_m^2(\mathbf{H}, T) + \lambda^2(T)$. Here Γ_m is the contribution due to the sample magnetization (a term proportional to H), and λ is the new contribution to the linewidth that vanishes above T_N.

Separating Γ into two components is compelled by its field dependence, which we present in Fig. 2. For $\mathbf{H} \perp \mathbf{c}$ and $T \sim 14.5$ K, Γ (open circles) increases slowly above about 3–4 T and is field independent below this value, with a clear nonzero intercept. The two-component fit is indicated by the curve [i.e., $\lambda(14.5\ \mathrm{K}) \sim 7$ G]. For comparison, at $T = 20$ K (filled circles) no extra width exists; the dashed curve is a straight-line fit (slope ~ 0.6 G/T). Similarly, the filled triangles in Fig. 2 give the total width for $\mathbf{H} \parallel \mathbf{c}$ and $T = 20$ K. Here the slope ($\sim$6.4 G/T) (dashed-line fit) is more than 10 times greater than for $\mathbf{H} \perp \mathbf{c}$ due to the large magnetic anisotropy of the system. The open triangles and squares give data obtained for $\mathbf{H} \parallel \mathbf{c}$ at $T = 14.5$ and 4.2 K, respectively. As for $\mathbf{H} \perp \mathbf{c}$, the curves drawn through these data are fits to a two-component Γ. It is seen from these fits that the orientation dependence of λ at constant T is weak or nonexistent; for example, at 14.5 K the fits are consistent with the same intercept: $\lambda(\mathbf{H} \perp \mathbf{c}, 14.5\ \mathrm{K}) \sim \lambda(\mathbf{H} \parallel \mathbf{c}, 14.5\ \mathrm{K}) \sim 7$ G. The value of λ at 4.2 K is clearly larger; $\lambda(4.2\mathrm{K}) \sim 13(2)$ G (see also Fig. 4 below). Finally, one can see from Fig. 2 why, in early NMR experiments, λ was not detected for high $\mathbf{H} \parallel \mathbf{c}$ [12] or for poorly aligned samples [13]. Because of the strong magnetic anisotropy in this system, the part of the width due to either the magnetization in the aligned powder or the anisotropic residual powder pattern in poorly aligned samples can overwhelm λ, even for low values of $\mathbf{H} \parallel \mathbf{c}$.

The Knight shift K has been reported previously for $\mathbf{H} \parallel \mathbf{c}$ and $\mathbf{H} \perp \mathbf{c}$ [12,13]. Since in AF systems one might expect a change in the orientation dependence of K as T crosses T_N [17], we followed K vs θ, the field orientation angle, above and below T_N. We find that the behavior of K reflects only the anisotropic magnetization and does not seem to be involved in the linewidth effect we observe: the line shape (Lorentzian-like) does not change with θ (Fig. 1), and neither the shift nor its anisotropy changes anomalously through T_N. This can be seen clearly in Figs. 3(a) and 3(b) where we present, respectively, $K(\theta)$ and $\Gamma(\theta)$ above ($T = 20$ K, open circles) and below ($T = 4.2$ K, closed circles) T_N. For both temperatures, the shift can be fit to $K = \cos^2\theta K_{\parallel}(T) + \sin^2\theta K_{\perp}$, (curves), as expected from crystal anisotropy. The difference in magnitude of K for $\theta \to 0$ is due to the temperature dependence of the magnetization in that direction.

The curve drawn in Fig. 3(b) for $T = 20$ K is expected if Γ represents a distribution of anisotropic shifts with two independent width components: $\Gamma_{\parallel}(T)$ and $\Gamma_{\perp}$. We find $\Gamma_{\parallel}(20\ \mathrm{K}) = 8.2 \pm 0.5$ G and $\Gamma_{\perp} = 1.9 \pm 0.5$ G.

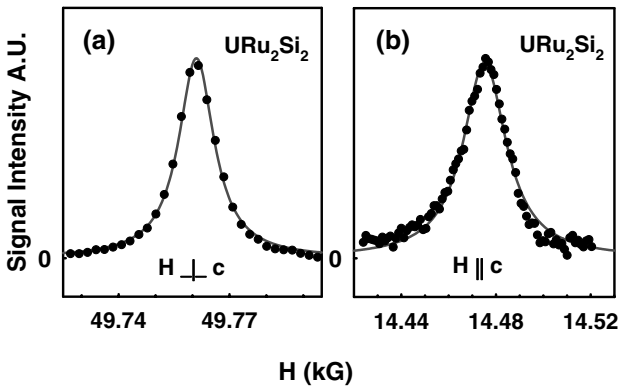

FIG. 1. ^{29}Si NMR spectra in URu_2Si_2 at $T = 14.5$ K for (a) $\mathbf{H} \perp \mathbf{c}$ and (b) $\mathbf{H} \parallel \mathbf{c}$. Curves: fits to Lorentzian functions of HWHM $\Gamma(\mathbf{H}, T)$.

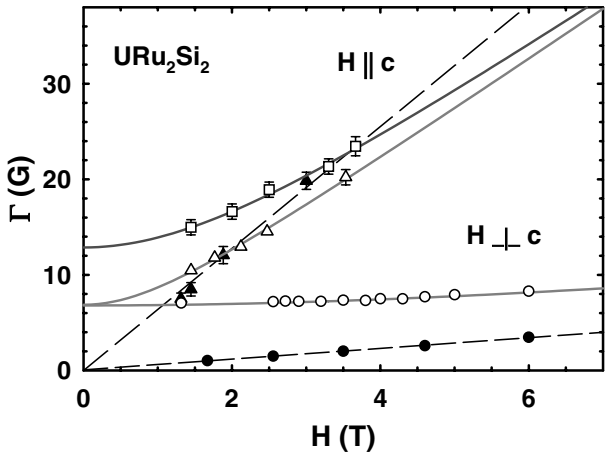

FIG. 2. Field dependence of the ^{29}Si linewidth Γ in URu_2Si_2. Circles: $\mathbf{H} \perp \mathbf{c}$, $T = 14.5$ K (open) and $T = 20$ K (filled). Filled triangles: $\mathbf{H} \parallel \mathbf{c}$, $T = 20$ K. Open triangles: $\mathbf{H} \parallel \mathbf{c}$, $T = 14.5$ K. Squares: $T = 4.2$ K. Curves: one- (dashed) and two- (solid) component fits to the linewidth.

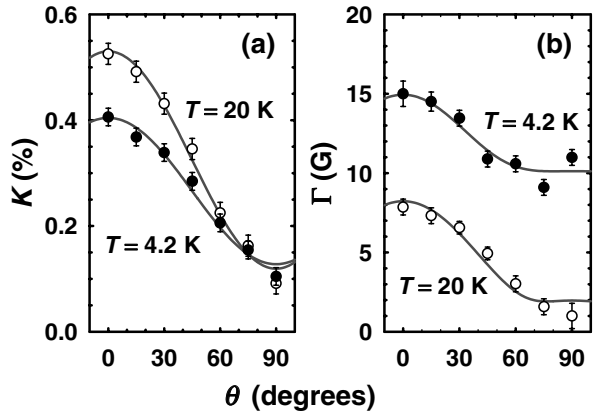

FIG. 3. Dependence of ^{29}Si Knight shift $K(T)$ (a) and linewidth $\Gamma(H = 1.45\ \mathrm{T}, T)$ (b) on c-axis angle θ in URu_2Si_2. Curves: fits to dependences (see text).

For $T = 4.2$ K [Fig. 3(b), closed circles], λ is nonzero. The curve shown is obtained by assuming that λ is isotropic and $\Gamma_\perp$ temperature independent. The fit gives $\Gamma_\parallel(4.2\ \mathrm{K}) = 11.3 \pm 1$ G and $\lambda(4.2\ \mathrm{K}) = 9.9 \pm 0.5$ G. On the other hand, the field dependence study (Fig. 2) suggests that λ can be as large as 13 G for $\mathbf{H} \parallel \mathbf{c}$. With $\lambda \sim 10$ G for $\mathbf{H} \perp \mathbf{c}$, the combined data from Figs. 2 and 3(b) put a 30% upper bound to the anisotropy of λ.

Figure 4 gives the temperature dependence of λ. The filled symbols are obtained for $\mathbf{H} \perp \mathbf{c}$ by direct quadrature subtraction of the term Γ_m, which is temperature independent for this field direction. Since Γ_m is strongly T dependent for $\mathbf{H} \parallel \mathbf{c}$, direct extraction of λ from the temperature dependence of the total width Γ in that geometry is not straightforward. We subtracted $\Gamma_m(\mathbf{H} \parallel \mathbf{c}, T)$ in this case by using the data of Fig. 2 together with a scaling of the form $\Gamma_m(\mathbf{H} \parallel \mathbf{c}, T) \propto M(\mathbf{H} \parallel \mathbf{c}, T)$, where M is the magnetization. The results are consistent with the lack of strong anisotropy inferred above from field and orientation studies. The behavior of λ clearly signals a coupling

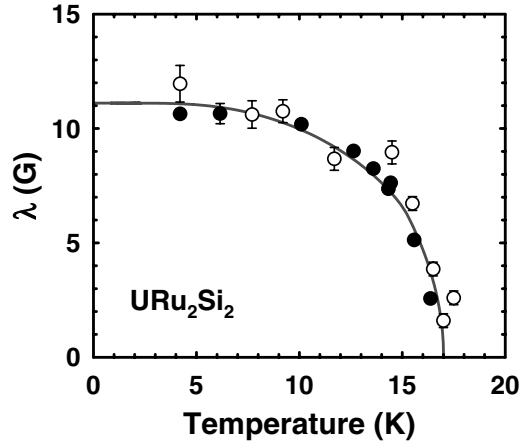

FIG. 4. Anomalous linewidth component $\lambda(T)$ extracted from ^{29}Si NMR in URu_2Si_2 for $\mathbf{H} \perp \mathbf{c}$ (filled circles) and $\mathbf{H} \parallel \mathbf{c}$ (open circles). Curve: fit to $S = 1/2$ mean-field order parameter.

between the bulk (paramagnetic-phase) ^{29}Si nuclear spins and the electronic transition at T_N. This is further corroborated by the excellent $S = 1/2$ mean-field order-parameter fit to $\lambda(T)$ (curve in Fig. 4).

Next, we discuss our results within two possible scenarios, neither of which turns out to be satisfactory: (i) disordered U-moment freezing, and (ii) inhomogeneous antiferromagnetism.

(i) If the distribution of effective fields were produced by disorder or incommensuration (due to a spin-density wave) in the direct (dipolar) or indirect transferred interaction between U moments and the ^{29}Si nuclei, then the line shape and width should be strongly anisotropic, reflecting the anisotropic coupling. There is no strong dependence of the line shape or λ on field orientation, even though the shift K does follow the anisotropic susceptibility. To account for this, a model of disordered magnetic freezing at the U sites would need to invoke a *continuous* distribution (with temperature independent shape) of moment sizes, in domains that include moment values all the way down to zero and nearly isotropic internal field orientations. Furthermore, essentially all U moments would have to be frozen. Such interpretation would be in striking contrast with ND [2] and μSR [14,18] measurements, which indicate that the magnetic correlations lie predominantly along the c axis, and with the pressure dependent inhomogeneous behavior described above [10,11].

(ii) Luke *et al.* [14] carried out μSR experiments which revealed sample-dependent IAF, presumably at ambient pressure, with a maximum AF volume fraction $\sim$10% and $\mu \sim 0.1\mu_B$/U ion. We associate this effect with the shoulders we sometimes see in ^{29}Si spectra [Fig. 1(d) of Ref. [12]], which can take as much as 15% of the spectral area. But these features do not reproduce reliably, suggesting that the IAF effect, besides being sample dependent [14], might also depend on conditions such as cooling and applied-field history. The major role of IAF in our measurements appears to be in the data scatter (10%–15%) observed, e.g., for $\Gamma(T = 4.2\ \mathrm{K}; \theta \sim 90°)$; Fig. 3(b). In contrast, the systematics and magnitude of λ are very insensitive to initial conditions, suggesting that λ itself is not due to this effect.

Nevertheless, let us assume that $\sim$10% of the sample is ordered in AF clusters as suggested in Ref. [14]. Now ND Bragg peak widths indicate a range of AF order of $\sim$100 lattice planes [2]; we take this distance as a minimum cluster size. Then only very small fields will be felt by most of the remaining 90% of the nuclei outside the clusters, because these nuclei are typically hundreds of lattice parameters from the nearest cluster; at such distances long-range dipolar or transferred hyperfine couplings cancel between the two AF sublattices. Thus at most 10% of the ^{29}Si nuclei experience appreciable local fields due to the AF order.

But large frequency shifts of 10% of the nuclei cannot explain the observed behavior of the linewidth. For example, for $\mathbf{H} \perp \mathbf{c}$ Γ increases from $\sim$2 G at 20 K to $\sim$10 G at 4.2 K [Fig. 3(b)], about a factor of 5. Thus

~80% of the spectral area must be redistributed from the center to the tails of the spectrum, whereas by hypothesis only ~10% is available from the AF clusters. A smaller AF volume fraction ($\lesssim$1% in Ref. [11]) only increases the strength of this argument. Thus, in contrast to Ref. [11], we conclude that combined NMR, ND, and μSR experiments rule out static magnetic freezing and inhomogeneous AF order as sources of the extra linewidth.

As a more viable possibility, Chandra *et al.* [16] have suggested orbital antiferromagnetism as the hidden order and the source of the extra ^{29}Si linewidth. In this picture, the order parameter ψ naturally breaks time-reversal invariance; the NMR linewidth is due to a distribution of fields produced by electronic currents running along U-U bonds in (a, b)-plane plaquettes. The current along the bonds is given by $I = e\Delta/\hbar$, where Δ is the gap associated with ψ [16]. For a plaquette of size a, the field induced at a height a above the plaquette (i.e., at the ^{29}Si site) is $B \sim (\mu/2\pi a)(e\Delta/\hbar)$. Using $a = 4 \times 10^{-10}$ m, $\Delta = 110$ K [1–3], the resulting current $I = 2.3$ μA, and $B = 11$ G, in excellent agreement with our measurements. The field distribution can be anisotropic in general, but is isotropic for a specific orbital antiferromagnetic wave vector $\mathbf{Q} = [1/4, 1/4, 1]$.

Alternatively, λ could be due to an indirect nuclear spin-spin interaction between unlike nuclei: $\mathcal{H}_{ij} = A_{ij}\mathbf{I_i} \cdot \mathbf{I_j}$, mediated by the coupling [7] between primary ψ and the secondary m order parameters. For instance, λ is static and inhomogeneous, so it represents a distribution of time-average-effective local fields such as could be produced by ^{99,101}Ru nuclei at ^{29}Si sites (like-spin ^{29}Si-^{29}Si interactions do not broaden the line). For low-natural-abundance nuclei this mechanism does not contribute to the shift K, which would explain the insensitivity of K to the 17 K transition. The field independence of λ would also be explained by this mechanism; the indirect interaction is a second-order effect, dominated by the excitation energy of the mediating electrons, which is in general much larger than the nuclear Zeeman energy. The mechanism itself would require that a ^{99,101}Ru nucleus produce a virtual excitation of the hidden-order state (which could be a quadrupolar or charge-density wave excitation governed by ψ). A change in the hidden-order spin state could then occur, which could be detected by nearby ^{29}Si nuclei. Qualitatively, this picture seems reasonable, but A_{ij} needs to be nearly isotropic, and a more quantitative description is not available. Perhaps calculations of this quantity based on proposed microscopic models (e.g., Ref. [9]) can be performed for comparison.

In conclusion, magnetic U-site spin freezing and simple IAF can be ruled out as sources of the anomalous linewidth λ, leaving the primary hidden order parameter ψ as the most likely cause. From the suggested pictures, orbital antiferromagnetism stands out as a very promising way to understand our results. The indirect nuclear coupling scenario could be tested by double resonance experiments, in which the unlike-spin nuclei are decoupled, and by NMR in isotopically enriched samples. NMR in U/Th and U/Y substituted alloys should also be performed.

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