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Nuclear quadrupole resonance and heavy-fermion superconductivity in $CeCu_2Si_2$

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^{63}Cu nuclear quadrupole resonance (NQR) has been observed in the ternary compound $CeCu_2Si_2$ which, when stoichiometric, is a heavy-fermion superconductor. In a superconducting specimen ($T_c \simeq 0.6$ K) the observed temperature dependence of the spin-lattice relaxation rate $1/T_1(T)$ is consistent with a conventional quasiparticle excitation spectrum below T_c, with a pair-breaking parameter approximately half the value for suppression of superconductivity. Features in $1/T_1(T)$ between T_c and 1.2 K appear to signal a phase transition, possibly structural in nature. NQR data from a nonsuperconducting sample are consistent with extensive disorder in the Cu site occupation.

I. INTRODUCTION

Unusual superconducting behavior has recently been discovered in several lanthanide and actinide compounds,[1-4] which exhibit enormous values of the low-temperature magnetic susceptibility χ and coefficient γ of the linear term in the specific heat. Enhanced electron masses $m^* \sim 100 m_e$ result from standard analyses of χ and γ, but the ratio χ/γ retains a value appropriate to a free-electron gas. It is of interest to obtain as much microscopic information as possible on both the normal and superconducting states of these so-called "heavy-fermion superconductors," in order to determine if their superconductivity is of a conventional kind or is due to some exotic mechanism.[5]

Nuclear quadrupole resonance (NQR) experiments in zero applied field can be carried out in favorable cases (site symmetry lower than cubic, nuclear spin $I > \frac{1}{2}$, large enough NQR frequency ω_Q). Zero-field NQR is ideal for measurements in the superconducting state:[6] only the radio-frequency (rf) field need penetrate the sample, and this penetration does not have to be homogeneous. The longitudinal (spin-lattice) relaxation rate $1/T_1$ is related to the fluctuation noise spectrum $J(\omega)$ of nuclear local-field fluctuations at $\omega = \omega_Q$. The transverse (spin memory) relaxation rate $1/T_2$ reflects contributions from $J(\omega)$ ($\omega = 0$ and $\omega = \omega_Q$) and from dipolar interactions between nuclei. The NQR signal amplitude and resonance linewidth $1/T_2^*$ are related to the distribution of static inhomogeneities in ω_Q.

In this Rapid Communication we report ^{63}Cu ($I = \frac{3}{2}$) NQR experiments in the ternary compound $CeCu_2Si_2$. It is now generally agreed that stoichiometric $CeCu_2Si_2$ is a heavy-fermion superconductor,[1] with a transition temperature T_c in the range 0.5–0.7 K. Because of the possibility of unusual superconducting behavior in this material it is desirable to obtain microscopic information from the superconducting state, and the present experiments were motivated by this consideration. The properties of $CeCu_2Si_2$ depend strongly on specimen preparation, however, and it is essential to correlate the results of any experiment with the nature of any defects (lack of stoichiometry, impurities, etc.) known to be present.

II. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

One superconducting sample (No. 1) and one nonsuperconducting sample (No. 3) were studied. Sample No. 1 was prepared in polycrystalline form. It was used in a previously reported study of ^{29}Si NMR in the normal state,[7] where a description of its preparation has been given. Sample No. 3 was grown as a single crystal from a liquid indium flux, and was stoichiometric to within $\pm 5\%$ (Ref. 8). It should be noted, however, that Cu deficiencies as small as 2% have been reported to suppress superconductivity severely.[9] Both samples were powdered and sieved to < 90 μm, and neither was heat treated after powdering. An ac susceptibility technique was used to detect the onset of superconductivity. Sample No. 1 exhibited a sharp superconducting transition at $T_c = 0.60 \pm 0.03$ K, with no precursor diamagnetism above this temperature to better than 10^{-3} the signal change at T_c. Sample No. 3 showed no superconductivity down to 0.35 K, the limit of our ^3He evaporation cryostat.

Conventional pulsed nuclear resonance techniques were used to measure longitudinal relaxation times T_1, spin-echo decay times T_2, and inhomogeneous linewidths $1/T_2^*$ at the ^{63}Cu ($I = \frac{3}{2}$) NQR frequency $\omega_Q/2\pi = 3.43$ MHz. Care was taken to avoid pulse heating of the sample at the lowest temperatures. Linewidths were obtained from the width of the spin echo, and resolution of wide lines was limited somewhat by the spectrometer bandwidth.

III. EXPERIMENTAL RESULTS

Figure 1(a) gives the temperature dependence of $1/T_1$ for the superconducting sample (No. 1). Data obtained from $LaCu_2Si_2$ are also shown for comparison. At a given temperature $1/T_1$ in $CeCu_2Si_2$ is much faster than in $LaCu_2Si_2$, which shows that Ce-derived wave functions dominate relaxation in the former compound.

The behavior of $1/T_1$ near T_c is similar to that in conventional superconductors,[6] where a maximum is found just below T_c from the increased BCS density of states of quasiparticle excitations just above the gap edge. The increase of $1/T_1$ for decreasing T seems to set in at about 0.65 K, which is somewhat higher than the ac susceptibility transition. (Similar ambiguities in T_c are generally found in comparisons of T_c from other techniques.) The height of the maximum in $1/T_1$ is reduced below that found in BSC-like superconductors, however. One mechanism for this reduction is pair breaking, which rounds off the BCS peak in the density of states.[6] From the observed reduction and the Ambegaokar-Griffin theory[6,10] one can estimate a pair-breaking parameter $\alpha/\alpha_{cr} \sim 0.5$ just below T_c, where α_{cr} is the critical value for complete suppression of superconductivity.

The rapid decrease of $1/T_1$ below ~ 0.55 K is consistent with the opening out of a gap ω_g in the quasiparticle spectrum. A fit of the Arrhenius law $1/T_1 \propto \exp(-\omega_g/k_B T)$ to the data, shown in Fig. 1(a), yields a value of $\omega_g = 1.15 \pm 0.1$ K, or $\omega_g/T_c = 1.92 \pm 0.17$. This result is consistent with the BCS value $\omega_g/T_c = 1.76$ in the absence of pair breaking. It disagrees somewhat with the Ambegaokar-Griffin theory, for which a fit of $1/T_1(T)$ to

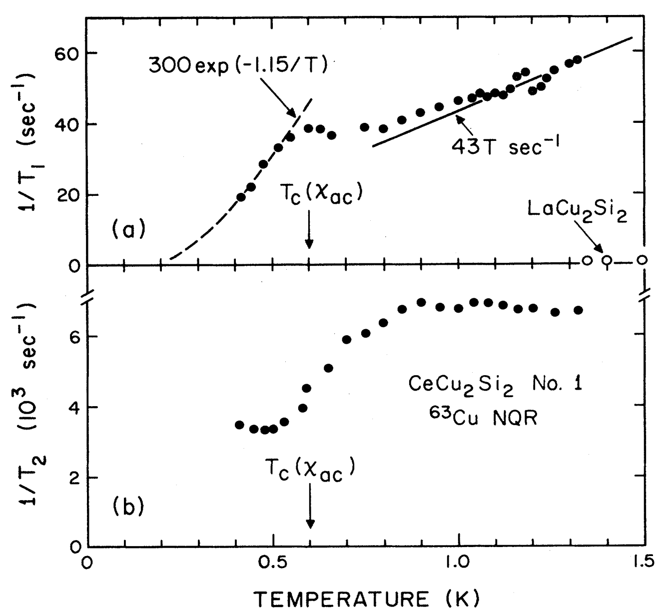

FIG. 1. (a) Temperature dependence of ^{63}Cu NQR longitudinal (spin-lattice) relaxation rate $1/T_1$ in normal and superconducting $CeCu_2Si_2$ (sample No. 1). Data from $LaCu_2Si_2$ are also shown for comparison. Solid line: best fit to normal-state Korringa law $1T_1 \propto T$ above ~ 1 K. Dashed curve: best fit to Arrhenius law $1/T_1 \propto \exp(-\Delta/T)$ below ~ 0.55 K. (b) Temperature dependence of ^{63}Cu NQR transverse relaxation rate $1/T_2$ in $CeCu_2Si_2$ (sample No. 1).

an Arrhenius law over the same temperature range yields $\omega_g/T_c \simeq 1.5$ for $\alpha/\alpha_{cr} = 0.5$. An unambiguous discrepancy cannot be claimed, however. Relaxation measurements at lower temperatures might help to resolve this question. In any event, it is not clear that $CeCu_2Si_2$ is expected to be a BCS superconductor with temperature-independent pair breaking.[11]

Above T_c the spin-lattice relaxation data show two anomalous features. First there is a sharp anomaly in $1/T_1$ at ~ 1.2 K [Fig. 1(a)] which is well outside the error bars of the measurement. This anomaly is also found in other superconducting specimens of $CeCu_2Si_2$, and does not seem to be an experimental artifact. (The situation for a nonsuperconducting specimen will be discussed below.) Second, $1/T_1(T)$ is not well described by the Korringa relation $1/T_1 \propto T$ between T_c and 1.3 K [Fig. 1(a)], as would be expected from a Fermi-fluid description of the low-tempeature state of the system.

In the absence of other hypotheses we speculate that these features are due to a phase transition, possibly structural in nature. (Specific-heat data exhibit no such anomaly in the same temperature region.) Further experiments, e.g., x-ray diffraction, would be helpful in elucidating this behavior. It should be noted that apart from the 1.2 K anomaly the normal-state data below 1.3 K can be fit to the functional form $1/T_1 = A + BT$. This has been previously observed in conventional metals containing dilute paramagnetic impurities,[12] where it was attributed to a combination of Korringa relaxation and the direct impurity contribution to the fluctuating nuclear local field.

Figure 1(b) gives the temperature dependence of the transverse relaxation rate $1/T_2$ in sample No. 1. A decrease of $1/T_2$ with decreasing temperature is observed below ~ 0.9 K. This does not seem to be due to the onset of superconductivity at 0.6–0.65 K, since no diamagnetism was observed above 0.6 K in the ac susceptibility, and may be another effect of the assumed phase transition. Microscopic strains, arising from an incomplete structural transitions, could "detune" neighboring nuclei and render their mutual dipolar interactions less effective in inducing mutual spin flips. We note that a large ($\times 2$) increase of $1/T_2$ has been observed very recently[13] in the superconducting state of the heavy-fermion superconductor UBe_{13}, but no such increase is evident in Fig. 1(b).

The temperature dependence of the ^{63}Cu spin-echo signal amplitude S_{se} (normalized to sample mass), with the nuclear Curie-law temperature dependence removed by forming the product TS_{se}, is given in Fig. 2(a) for both superconducting and nonsuperconducting samples. The significant loss of signal observed below T_c for sample No. 1 can be partially attributed to expulsion of the rf field in the superconducting state: only nuclei within the order of a London penetration depth of the particle surfaces are observed. Signal reduction is also observed above $T_c(\chi_{ac})$, and even above the local minimum in $1/T_1$ at ~ 0.66 K (Fig. 1). This is also consistent with the presence of an incomplete structural transition, which could lead to a distribution of electric field gradients and wipeout of ^{63}Cu nuclei from the NQR signal. We reemphasize that in this temperature range there is no indication of superconducting diamagnetism in the ac susceptibility.

NQR signal amplitude measurements in the nonsuperconducting sample (No. 3) show no appreciable variation in TS_{se} down to 0.35 K, which is consistent with the absence

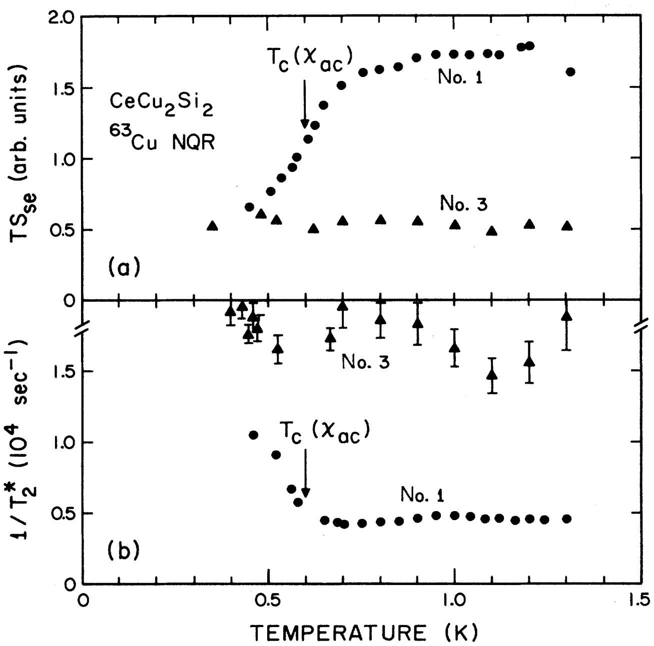

FIG. 2. (a) Product TS_{se} of temperature and the ^{63}Cu NQR spin-echo signal amplitude S_{se} (normalized to sample mass) in superconducting (No. 1, circles) and nonsuperconducting (No. 3, triangles) specimens of $CeCu_2Si_2$. (b) Temperature dependence of ^{63}Cu inhomogeneous linewidth $1/T_2^*$ in superconducting (No. 1, circles) and nonsuperconducting (No. 3, triangles) specimens of $CeCu_2Si_2$. The data for sample No. 3 are limited by the spectrometer bandwidth, and give only a lower bound on $1/T_2^*$.

of a superconducting transition in the ac susceptibility. But the most striking result is the loss of signal in the normal state relative to sample No. 1. A correspondingly large inhomogeneous linewidth $1/T_2^*$ is also observed in sample No. 3 relative to sample No. 1, as shown in Fig. 2(b). These data suggest that in nonsuperconducting sample No. 3 the copper sublattice is considerably less perfect than in superconducting sample No. 1. This is in accord with evidence[9] that the absence of superconductivity can be correlated with the presence of defects, particularly in the Cu sublattice. The reduced signal strength in sample No. 3 means that the observed resonance is representative only of nuclei in unstrained regions of the specimen. No sharp $1/T_1$ anomaly at 1.2 K was observed in sample No. 3, but the signal-to-noise ratio for this sample was poor, and resolution of the anomaly would have been difficult even if it were present. The significance of this result is unclear, however, because of the unrepresentative nature of the nuclear signal. The increase of $1/T_2^*$ in sample No. 1 below T_c could be due either to inhomogeneous magnetic fields (possibly from trapped flux), or to inhomogeneous electric field gradients near powder grain surfaces.

IV. CONCLUSIONS

Nuclear quadrupole resonance experiments in the normal and superconducting states of $CeCu_2Si_2$ have revealed a number of features. The superconducting behavior is consistent with a conventional kind of superconductivity and pair breaking, although this interpretation is by no means unique. There is no evidence for the relaxation by slow magnetic fluctuations that has been observed[13] in the mixed state of the heavy-fermion superconductor UBe_{13}. There appears to be a transition, possibly structural in nature, at temperatures above T_c. NQR in a nonsuperconducting specimen reveals the presence of considerable disorder in the copper sublattice.

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[1]F. Steglich, J. Aarts, C. D. Bredl, W. Lieke, D. Meschede, W. Franz, and H. Schafer, Phys. Rev. Lett. **43**, 1892 (1979).

[2]H. R. Ott, H. Rudigier, Z. Fisk, and J. L. Smith, Phys. Rev. Lett. **50**, 1595 (1983).

[3]L. E. DeLong, J. G. Huber, K. N. Yang, and M. B. Maple, Phys. Rev. Lett. **51**, 312 (1983).

[4]G. R. Stewart, Z. Fisk, J. O. Willis, and J. L. Smith, Phys. Rev. Lett. **52**, 679 (1984).

[5]C. M. Varma, Bull. Am. Phys. Soc. **29**, 404 (1984); P. W. Anderson (unpublished).

[6]See, e.g., D. E. MacLaughlin, Solid State Phys. **31**, 1 (1976).

[7]J. Aarts, F. R. de Boer, and D. E. MacLaughlin, Physica B **121**, 162 (1983).

[8]G. R. Stewart, Z. Fisk, and J. O. Willis, Phys. Rev. B **28**, 172 (1983).

[9]M. Ishikawa, H. F. Braun, and J. L. Jorda, Phys. Rev. B **27**, 3092 (1983); H. Spille, U. Rauchschwalbe, and F. Steglich, Helv. Phys. Acta **56**, 165 (1983).

[10]V. Ambegaokar and A. Griffin, Phys. Rev. **137**, A1151 (1965); A. Griffin and V. Ambegaokar, in *Low Temperature Physics (LT-9)*, edited by J. G. Daunt *et al.* (Plenum, New York, 1965), Pt. A, p. 524.

[11]C. D. Bredl, H. Spille, U. Rauchschwalbe, W. Lieke, F. Steglich, G. Cordier, W. Assmus, M. Herrmann, and J. Aarts, J. Magn. Magn. Mater **31–34**, 373 (1983).

[12]D. E. MacLaughlin, J. Low Temp. Phys. **26**, 111 (1977).

[13]G. W. Clark, Z. Fisk, K. Glover, M. D. Lan, D. E. MacLaughlin, J. L. Smith, and C. Tien (unpublished).