Muon Spin Relaxation Studies of Superconductivity in a Crystalline Array of Weakly Coupled Metal Nanoparticles

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(Received 19 May 2006; published 15 August 2006)

We report muon-spin-relaxation studies in weak transverse fields of the superconductivity in the metal cluster compound, $Ga_{84}[N(SiMe_3)_2]_{20}$-$Li_6Br_2(thf)_{20} \cdot 2$ toluene. The temperature and field dependence of the muon-spin-relaxation rate and Knight shift clearly evidence type II bulk superconductivity below $T_c \approx 7.8$ K, with $B_{c1} \approx 0.06$ T, $B_{c2} \approx 0.26$ T, $\kappa \sim 2$, and weak flux pinning. The data are well described by the s-wave BCS model with weak electron-phonon coupling in the clean limit. A qualitative explanation for the conduction mechanism in this novel type of narrow-band superconductor is presented.

The chemical synthesis of molecular metal cluster compounds presents an attractive bottom-up route for the generation of self-organized nanostructures composed of 3D ordered arrays of identical metal nanoparticles embedded in a dielectric matrix. Until recently, such cluster solids were always found electrically insulating. On the other hand, the strong similarity with (super)conducting molecular crystals, as the alkali-metal-doped fullerenes (C_{60}), suggests that, in principle, metal cluster compounds could also display metallic conductivity (and even superconductivity) due to intermolecular charge transfer. We have indeed recently obtained compelling evidence from ^{69,71}Ga-NMR [1] and magnetization measurements for the occurrence of *band-type conductivity* in crystalline ordered Ga_{84} cluster compounds, composed of arrays of giant Ga_{84} cluster molecules that display mixed-valence properties. In addition, *bulk type II superconductivity* was observed below a transition temperature $T_c \approx 7.5$ K, much higher in fact than known for bulk α-Ga metal ($T_c \approx 1$ K). This material may thus represent a first experimental realization of a theoretical model advanced by Friedel in 1992 [2], who predicted that for a *crystalline array of identical metal nanoparticles*, a very weak interparticle charge transfer can still yield superconductivity with a relatively high T_c value.

From the NMR study, a number of results were obtained. First, the field and temperature dependence of the Knight shift can be well fitted to BCS theory for weak electron-phonon coupling, a rather surprising result since strong correlations would be expected for such narrow-band conductors as the present. Second, a very strong sample dependence of the second critical field B_{c2} was revealed. As compared to $B_{c2} \approx 13.8$ T reported previously [3], we found that for most of the samples the minimum field of about 2 T required for the NMR signal (due to signal-to-noise ratio) was already sufficient to suppress the superconductivity completely. Only in a few samples superconductivity could be detected by NMR up to about 5 T. By

contrast, magnetization studies showed diamagnetic signals for all samples below similar values of $T_c = 7$–8 K, but with apparent B_{c2} values as low as 0.3 T. Although an explanation of this variation (by a factor of 50) in terms of lattice defects—associated with orientational disorder in the molecular crystal lattice—was proposed, definite proof for the occurrence of bulk superconductivity in the low B_{c2} samples seemed highly desirable. In order to check this assumption, muon-spin-relaxation (μSR) experiments in small transverse fields (B_{TF}) have therefore been performed. As discussed below, they provide unambiguous proof for bulk type II superconductivity, with a Ginzburg-Landau (GL) parameter $\kappa \sim 2$, and are likewise in agreement with weak-coupling BCS model predictions. A qualitative discussion of the nature of the conduction mechanism in terms of intermolecular charge fluctuations is presented at the end of the Letter.

The crystal structure of the giant molecular cluster compounds Ga_{84}, which is short for $Ga_{84}[N(SiMe_3)_2]_{20}$-$Li_6Br_2(thf)_{20} \cdot 2$ toluene (Me $= CH_3$ and thf $= C_4H_8O$), is fully described in [4]. The μSR experiments were performed on the sample labeled S3 in the previous work [1], which showed an excellent crystallinity in x-ray experiments [4], with typical dimensions of the (randomly oriented) crystallites of 0.1 mm. Magnetization measurements in a commercial SQUID magnetometer evidence a superconducting (SC) transition at $T_c = 7.75(5)$ K in zero external field. A $T = 0$ extrapolation yields an upper critical field $B_{c2} \approx 0.26$ T. Using the expression $B_{c2} \approx \Phi_0/2\pi\xi^2$, where Φ_0 is the flux quantum, gives a coherence length $\xi \sim 35$ nm much larger than the intercluster distance, of order 2 nm. The extrapolated thermodynamical critical field at $T = 0$ was found as $B_{c1} \approx 60$ mT. Using the general expression given by Brandt for an ideal triangular GL vortex lattice, relating B_{c2}, B_{c1} and the GL parameter κ [5], we find $\kappa \sim 2$ and a London penetration depth $\lambda \sim 70$ nm. This sample, which is consequently close to the "clean" SC limit, indeed

displays the largest (super)conducting fraction reached so
far in a Ga_{84} sample (90%), as found in the $^{69,71}Ga$ NMR
experiments performed on several batches [1].

Transverse field μSR is a powerful technique to probe
type II superconductivity locally [6], and can be performed
in any arbitrary field close to zero, contrary to NMR. By
implanting 100% spin polarized muons (μ^+) in the mate-
rial, the local field they experience can be measured
through their decay into, among others, a positron, in a
typical time window of 0.1–10 μs. We performed our
experiments on the πM3 beam line on the GPS spectrome-
ter in PSI, Villigen, Switzerland, in the temperature range
2 K $\leq T \leq$ 10 K, using magnetic fields $0 \leq B_{TF} \leq 0.4$ T.
The Ga_{84} sample (30 mg) is extremely air sensitive and
must be kept in a toluene solution with a sample/toluene
mass ratio of order 80/20($\pm$10) to avoid loss of crystal
solvent. We therefore sealed it in an Al sample holder [7],
using an Al thickness of 0.35 mm between the incident μ^+
beam and the sample as a moderator for the muons. From
the geometry of our sample, a pellet of thickness 0.55 mm
and diameter 7 mm, and the calibrated beam distribution,
the μ^+ fraction stopped in the Al sample holder (plus the
nonconducting fraction of Ga_{84}) called "background" in
the following, is of order 25%. This will appear as a
temperature- and field-independent signal in the whole
temperature range. The μ^+ fraction stopped in toluene is
of order 17% and does not contribute to the measured
signal, as seen experimentally by a reduction of the ex-
pected intensity by this amount. We attribute this reduction
to the formation of muonium in this solvent. Given the
large fraction of muons stopping outside the superconduct-
ing Ga_{84} sample ($\sim$ 42%) we took data with good statis-
tics, with typically $40 \times 10^6 \mu^+$ per point.

Figure 1 shows the time dependence of the μ^+ polar-
ization $P(t)$ along the polarization axis, perpendicular to
B_{TF}, for two temperatures and $B_{TF} = 60$ mT $\gtrsim B_{c1}$, in a
field cooled (FC) experiment. A clear difference can be
seen between the data measured at $T = 10$ K $> T_c$ and
$T = 2$ K $\ll T_c$. Above T_c, the local field (B_μ) distribution
is small and only due to nuclear dipoles. It yields a usual
slow Gaussian depolarization and a precession frequency
centered at the suited Larmor frequency $\gamma B_\mu/2\pi$, where γ
is the μ^+ gyromagnetic ratio. Below T_c, a flux line lattice
(FLL) is created in the mixed state, resulting in a larger
distribution of B_μ, i.e, a faster relaxation of $P(t)$.

In order to get a first *qualitative* impression of the
behavior of the various relevant parameters, a single
damped cosine was fitted to the raw data. This model-
independent analysis already clearly shows a transition at
$T_c \approx 6.4$ and 5.9 K, for $B_{TF} = 60$ and 90 mT (correspond-
ing to B_{c2} found in magnetization measurements at these
temperatures), in a FC experiment, in both the relaxation
rate (not shown) and the precession frequency, ν_{tot}
[Fig. 2(inset)]. In a second step, the background contribu-
tion has to be evaluated to get more *quantitative* informa-
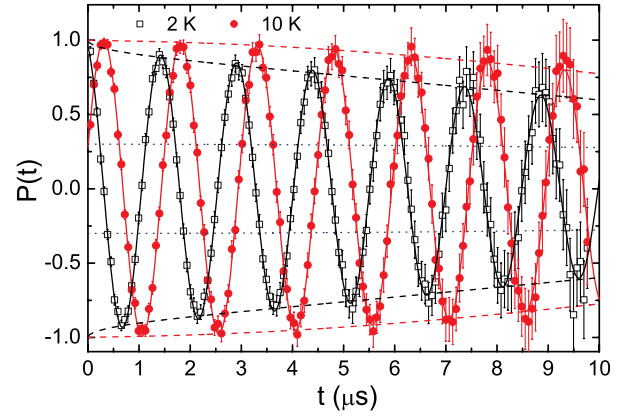tion. To fit the μ^+ polarization, we used the phenomeno-

FIG. 1 (color online). Polarization $P(t)$ of the μ^+ spins, in a
FC experiment ($B_{TF} = 60$ mT). For clarity, only one of the two
parts (imaginary or real) is presented for each T, in a rotating
frame at a frequency $\gamma \times 55$ mT. The continuous lines are fits
with Eq. (1). The dotted and dashed lines represent the envelope
of the background and the total signal, respectively.

logical function

$$P(t) = x \exp(-[\sigma_{Ga}t]^\alpha - \sigma_{nd}^2 t^2) \cos(\omega_{Ga}t + \phi)$$
$$+ (1 - x) \exp(-\sigma_{bgd}^2 t^2) \cos(\omega_{bgd}t + \phi). \quad (1)$$

The first term accounts for the Ga_{84} signal. The second
term represents the background. The relaxation rates σ_{nd}
and σ_{bgd} are due to the nuclear dipolar fields on the
respective sites [6]. A global fit was used, sharing the T-
and B_{TF}-independent parameters in order to limit the num-
ber of free parameters and to avoid unrealistic values. It
yields a fraction $x \approx 0.7$ of μ^+ stopping in Ga_{84}, $\sigma_{nd} \approx$
0.06 μs^{-1} and $\sigma_{bgd} \approx 0.04$ μs^{-1}, which are typical val-
ues for nuclear relaxation rates [6,8,9]. Although a rough
approximation, a Gaussian ($\alpha = 2$) is usually suited to fit
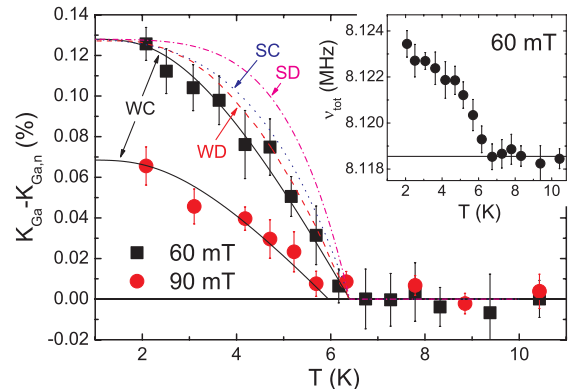

FIG. 2 (color online). T dependence of $K_{Ga} - K_{Ga,n}$, for two
values of B_{TF}. Lines are BCS fits with a s-wave symmetry of the
SC gap. Labels are weak (W) and strong (S) electron-phonon
coupling, and clean (C) and dirty (D) limits. Insets: precession
frequency ν_{tot} of the μ^+ spins obtained with a single damped
cosine fit, for $B_{TF} = 60$ mT. The line shows the average value
for $T > T_c$.

the FLL field distribution in powder samples [5,10]. This implies that the second moment of the field distribution, $\langle \Delta B_\mu^2 \rangle^{1/2}$, related to the penetration depth λ, is directly proportional to the μ^+ relaxation rate due to the FLL distribution (σ_{Ga}). In our case a Gaussian cannot account for the decay of the first $P(t)$ oscillations at low-T (Fig. 1) and we find instead a T- and B_{TF}-independent $\alpha \approx 0.5$. This value is reminiscent of inhomogeneous field distribution cases as in spin glasses [11]. Given the fact that a strong sample dependence of B_{c2} is found in Ga$_{84}$ [1], a distribution of B_{c2} in this particular sample is also possible and would explain this result. A complication of this α value is that the corresponding average field distribution does not converge unless a cutoff (which could not be measured within the experimental resolution) is introduced in the spectrum. To proceed, we therefore assume the proportionality $\sigma_{Ga}^2 \propto \langle \Delta B_\mu^2 \rangle$ to be still obeyed. We are then finally left with only two free parameters, σ_{Ga} and ν_{Ga}.

The T dependence of the average shift $K_{Ga} = (\omega_{Ga} - \gamma B_{TF})/\gamma B_{TF}$, is displayed in Fig. 2. This (muon) *Knight shift* is usually the sum of a T- and B_{TF}-independent orbital shift K_{orb} and a spin part K_S, proportional to the s-electron susceptibility [and to the electronic density of state at the Fermi level, $D(E_F)$]. In the normal state (n), we find a T- and B_{TF}-independent value (as expected in metals) of $K_{Ga,n} \sim K_{bgd} \sim -0.17\%$. The negative sign is due to the hyperfine coupling of the μ^+ with the carriers, which is known to be strongly sample dependent [12,13]. The present value is comparable to those found in several heavy fermion compounds [14,15].

Below T_c, the average precession frequency (inset of Fig. 2) is seen to increase continuously down to $T \rightarrow 0$ for both values of B_{TF}. Since the Knight shift is negative, this implies a decrease of its absolute value. In the mixed state, a possible additional shift (K_d) due to the demagnetization and Lorentz fields would reduce the local field at the muon site. Therefore, it cannot account for an increase of ν_{tot} and hence the variation of the shift can be attributed to a decrease of the spin part $|K_S|$ due to spin-singlet-pairing of the quasiparticles below T_c [16].

Figure 2 shows that $K_S(T)$ is well fitted by a BCS model with s-wave symmetry of the SC gap and weak electron-phonon coupling (i.e., with a SC gap $\Delta_0 \approx 1.76 k_B T_c$) [17,18]. The decrease of the SC carrier density due to the increase of B_{TF} is directly observed through a nonzero shift at $T \rightarrow 0$. It is also clear that the reduction of $|K_S|$ is larger in the "low" field measurement, as expected from a larger fraction of Cooper pairs [19]. The strong electron-phonon coupling and the dirty limit cases (the latter being unlikely from the magnetization data) [20] are also presented in Fig. 2. Their steeper variation below T_c clearly does not agree with the data.

The T dependence of σ_{Ga} is presented in the inset of Fig. 3. The reduction of T_c and an increase of the internal field homogeneity (i.e., a decrease of σ_{Ga}), is clearly observed when B_{TF} is increased. In the extensively studied

cuprates and heavy fermions, the conditions $\kappa \gg 1$ and $B_{TF} \ll B_{c2}$ imply that the ratio σ_{Ga}/λ^{-2} is roughly T and B_{TF} independent [6,9]. Here, the artificial reduction of σ_{Ga} due to the overlap of the vortices near B_{c2} has to be taken into account. In the framework of the GL theory, Brandt derived the quantity $\lambda^2 \langle \Delta B_\mu^2 \rangle^{1/2}$ as a function of κ and b, where b is the average internal field divided by $B_{c2}(T)$ [5]. Calling this quantity $f(b)$, the function $\lambda^{-2} \propto f(b)\sigma_{Ga}$ is presented in Fig. 3, taking $\kappa = 2$. The qualitative variation of $\lambda^{-2}(T)$ is very similar to the T dependence of K_S, as expected in the BCS model in small fields [17,18], and as shown by the fit with weak electron-phonon coupling in the clean limit (Fig. 3). This is quite rewarding concerning the validity of the analysis.

Next, we discuss the field dependence of σ_{Ga} at low T. We measured σ_{Ga} from the pure diamagnetic state up to the normal state by increasing the field from a zero field cooled (ZFC) condition at 2 K, from 0 up to $B_{TF} > B_{c2}$. The results of the fits with Eq. (1) are presented in Fig. 4. For small fields ($B_{TF} \lesssim B_{c1}$), σ_{Ga} continuously increases with B_{TF}. A strong inhomogeneity of the electron density of state in Ga$_{84}$, as well as the powder nature of the sample as suggested in [10], may lead to some FLL bending around SC grains and an inhomogeneity responsible for a nonzero σ_{Ga}. When $B_{TF} \gtrsim B_{c1}$, σ_{Ga} reflects both the FLL organization [5] and the field dependence of λ^{-2}. For high fields ($B_{TF} \gtrsim B_{c2} \sim 0.2$ T at 2 K), the superconductivity is destroyed and an homogeneous field ($\sigma_{Ga} = 0$) is recovered. The ratio $\lambda/\lambda(0) \propto [f(b)\sigma_{Ga}]^{-2}$ is presented in the inset of Fig. 4 as a function of b. In a BCS model with s-wave symmetry, the penetration depth λ is expected to be weakly field dependent [21], with a roughly linear variation of σ_{Ga}. However, a linear variation of λ, quantitatively comparable to the type II superconductor NbSe$_2$ [6], is measured and is consistent with a d-wave symmetry of the SC gap (continuous lines) [6,22]. Moreover, the predicted σ_{Ga} variation, with a constant λ, does not fit the data (dashed line). The theoretical computations are usually performed in an equilibrium FLL, which does not really correspond to our case. Indeed, the pinning of the vortices increases the local
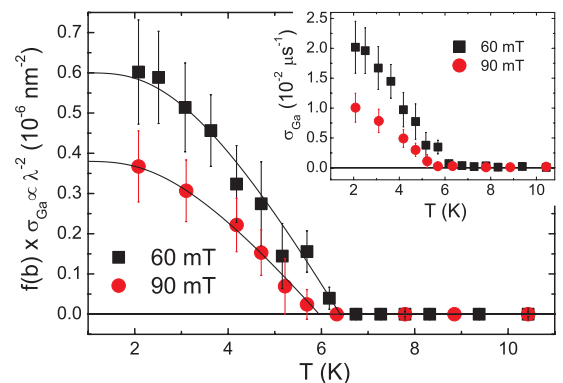

FIG. 3 (color online). T dependence of $f(b)\sigma_{Ga} \propto \lambda^{-2}$. The lines are BCS fits (WC). Inset: $\sigma_{Ga}(T)$ from Eq. (1).
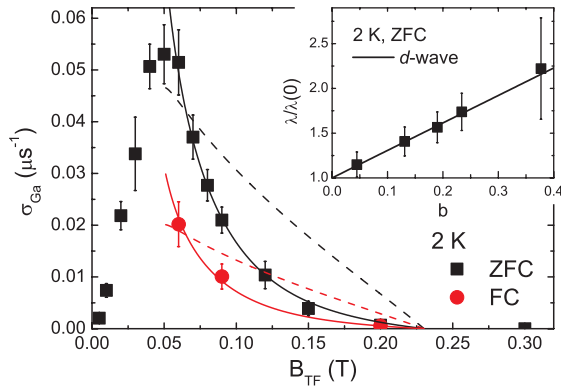
FIG. 4 (color online). B_{TF} dependence of σ_{Ga}, in ZFC and FC conditions. The pinning accounts for the difference. Inset: $\lambda(b)/\lambda(0)$. The lines are computations with $\kappa = 2$, a constant λ (s wave, dashed lines) and $\lambda/\lambda(0) \propto 1 + 3.1(5)b$ (d wave, solid lines). We note that $b = 0$ when $B_{TF} \leq B_{c1}$ [5].

field distribution, as seen by the usual [10,23] reduction of σ_{Ga} in the FC case (which also reduces the sensitivity of the experiment). However, the shape of the variation does not seem to be changed. We stress that these results should be taken with caution since the phenomenological function with $\alpha = 0.5$ could bias the results on σ_{Ga}, and λ. In any case the quantitative value for λ is uncertain.

Finally, we address the nature of the conduction mechanism in Ga_{84}. In the Friedel model, referred to in the introduction, conduction would occur in a narrow band originating from a molecular energy level near E_F of the Ga_{84} cluster, with a width proportional to the intercluster, i.e., anion-anion charge transfer t. In view of the ligand shells around the Ga_{84} cluster cores, t is, however, expected to be quite small, of order 0.01 eV. In a Hubbard model approach, t would have to compete with the on-site Coulomb interaction (Hubbard-U) of the anion, estimated at about 0.5 eV (3 times smaller than for C_{60}). In such a narrow-band system, strong electron-electron correlations are expected whereas the NMR and μSR experiments both indicate nearly free electron behavior (Korringa constants, Knight shifts). It appears relevant, therefore, to consider other possible charge fluctuations.

In analogy with the well-known models proposed for the transition metal compounds [24], one such possibility could be an electron transfer from the cluster anion to the Li cation, in combination with conduction in the cation band derived from the cation-cation overlap. Preliminary estimates, based on the cation ionization energy, the anion electron affinity, and the Madelung energies involved, indicate the anion-cation charge transfer process to be almost energetically neutral, i.e., it could in fact be quite small, smaller perhaps than the width of the cation band. The latter is difficult to estimate but could be larger than t. In this scenario the itinerant carriers would reside mainly in the cation band, which could explain why in the measured

Ga-NMR spectra the different Ga sites in the cluster are clearly resolved, as in an insulating Ga compound. Clearly, more sophisticated calculations are needed to further elucidate the conduction processes in this exciting novel type of molecular (super)conductor.

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