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We report Muon Spin Relaxation studies in weak transverse fields of the superconductivity in the metal cluster compound, $Ga_{84}[N(SiMe_3)_2]_{20}$-$Li_6Br_2(thf)_{20}$·2toluene. 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.

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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-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 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 paper.

The crystal structure of the giant molecular cluster compounds Ga_{84}, which is short for $Ga_{84}[N(SiMe_3)_2]_{20}$-$Li_6Br_2(thf)_{20}$·2toluene, is fully described in [4]. The μSR experiments were performed on the sample labelled S3 in the previous work [1], which showed an excellent crystallinity in x-ray experiments [4], with typical dimensions of the crystallites of 0.1 mm. Magnetization measurements in a commercial SQUID magnetometer evidence a 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 inter-cluster 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 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 material, 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 spectrometer in PSI, Villigen, Switzerland, in the temperature range 2 K $\leq T \leq$ 10 K, using magnetic fields $0 \leq B_{\rm TF} \leq 0.4$ 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$10) to avoid loss of crystal solvent. We therefore sealed it in an Al sample holder [22], using an Al thickness of 0.35 mm between the incident μ^+ beam and the sample as a moderator for the muons. From the geometry our sample, a pellet of thickness 0.55 mm and diameter 7 mm, and the calibrated beam distribution, the μ^+ fraction stopped in the Al sample holder (plus the non conducting fraction of Ga_{84}) called "background" in the following, is of order 25%. This will appear as a temperature- and field-independent signal in the whole temperature range. The μ^+ fraction stopped in toluene is of order 17% and does not contribute to the measured signal, as seen experimentally by a reduction of the expected intensity by this amount. We attribute this reduction to the formation of muonium in this solvent. Given the large fraction of "lost" muons ($\sim 42\%$) we took data with good statistics, with typically 40×10^6 μ^+ per point.

Figure 1 shows the time dependence of the μ^+ polarization $P(t)$ along the axis defined by B_{TF}, for two temperatures and $B_{\rm TF} = 60$ mT $\gtrsim B_{\rm c1}$, in a Field Cooled (FC) experiment. A clear difference can be seen between the data measured at $T = 10$ K $> T_{\rm c}$ and $T = 2$ K $\ll T_{\rm c}$. Above $T_{\rm c}$, the local field (B_μ) distribution is uniform in the sample and centered at the corresponding Larmor frequency $\gamma B_\mu/2\pi$, where γ is the μ^+ gyromagnetic ratio. In real time, the relaxation of $P(t)$ is therefore very slow. Below $T_{\rm c}$, 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 $T_{\rm c} \approx 6.4$ and 5.9 K, for $B_{TF} = 60$ and 90 mT (corresponding to $B_{\rm c2}$ found in magnetization measurements at these temperatures), in a FC experiment, in both the relaxation rate (not shown) and the precession frequency, $\nu_{\rm tot}$ [Fig 2(inset)]. In a second step, the background contribution has to be evaluated to get more *quantitative* information. To fit the μ^+ polarization, we used the phenomenological function

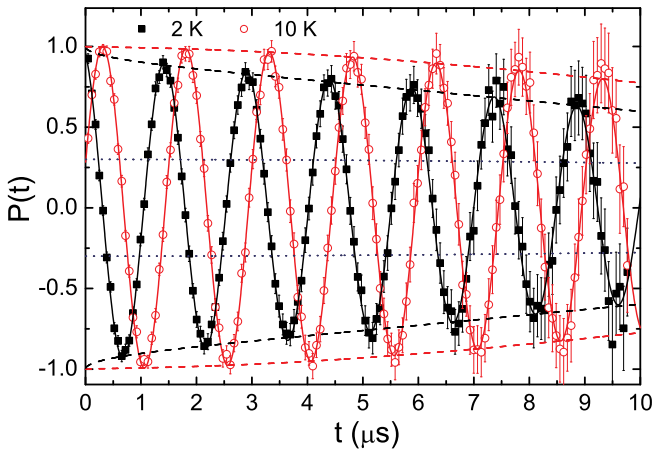

FIG. 1: Polarization $P(t)$ of the μ^+ spins, in a FC experiment ($H_{\rm TF} = 60$ mT). For clarity, only one of the two parts (imaginary or real) is presented for each T, in a rotating frame at a frequency $\gamma \times 55$ mT. The continuous lines are fits with Eq. 1. The dotted and dashed lines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

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

The first term accounts for the Ga_{84} signal. We point out that these μ^+ are likely stopped in the $Ga_{84}[N(SiMe_3)_2]_{20}^{4-}$ clusters, the other locations in the crystal corresponding to regions having a positive charge. The second term represents the background. The relaxation rates $\sigma_{\rm nd}$ and $\sigma_{\rm bgd}$ are due to the nuclear dipolar fields on the respective sites [6]. We first determined the T- and $B_{\rm TF}$-independent parameters by comparing all the data. The fits yield a fraction $x \approx 0.7$ of μ^+ stopping in Ga_{84}, $\sigma_{\rm nd} \approx 0.06$ μs^{-1} and $\sigma_{\rm bgd} \approx 0.04$ μs^{-1}, which are typical values for nuclear relaxation rates [6, 7, 8]. Although a rough approximation, a Gaussian ($\alpha = 2$) is usually suited to fit the FLL field distribution in powder samples [5, 9]. 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 ($\sigma_{\rm Ga}$). 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 $H_{\rm TF}$-independent $\alpha \approx 0.5$. This suggests a more complex FLL distribution [10] in this cluster compound. A complication of this α value is that the corresponding 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 $\sigma_{\rm Ga}^2 \propto \langle \Delta B_\mu^2 \rangle$ to be still obeyed. We are then finally left with only two

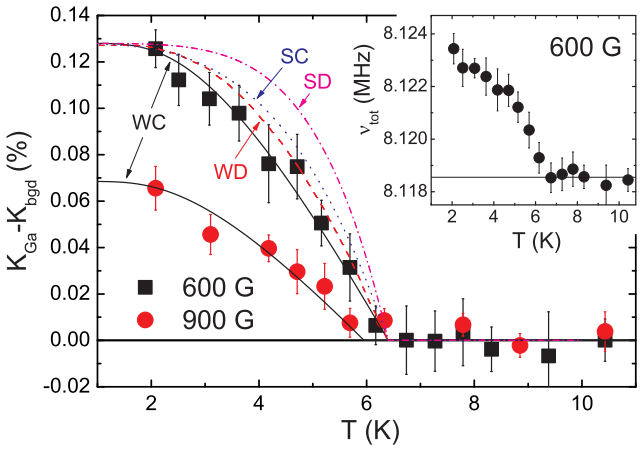

FIG. 2: T-dependence of $K_{\rm Ga} - K_{\rm bgd}$, for two values of $B_{\rm TF}$. Lines are BCS fits with a s-wave symmetry of the SC gap. "W" and "S" are for "weak" and "strong" electron-phonon coupling, "C" and "D" for "clean" and "dirty" limits. Insets: precession frequency $\nu_{\rm tot}$ of the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

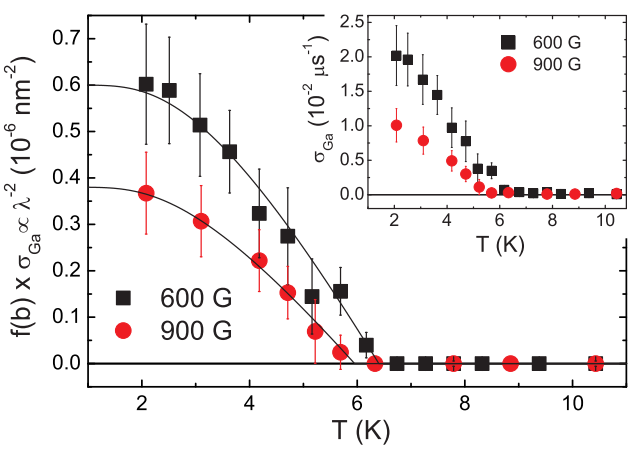

FIG. 3: T-dependence of $f(b)\sigma_{\rm Ga} \propto \lambda^{-2}$. The lines are BCS fits (WC). Inset: $\sigma_{\rm Ga}(T)$ from Eq. 1.

free parameters, $\sigma_{\rm Ga}$ and $\nu_{\rm Ga}$.

The T-dependence of the average shift $K_{\rm Ga} = (\omega_{\rm Ga} - \gamma B_{TF})/\gamma B_{TF}$, is displayed in Fig. 2 with the background shift $K_{\rm bgd}$ subtracted. This (muon) *Knight shift* is usually the sum of a T- and $B_{\rm TF}$-independent orbital shift $K_{\rm orb}$ 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 $B_{\rm TF}$-independent value (as expected in metals) of $K_{\rm Ga,n} \sim K_{\rm bgd} \sim -0.17\%$. The negative sign is due to the hyperfine coupling of the μ^+ with the carriers, which is known to be strongly sample dependent [11] [23]. The present value is comparable to those found in several heavy fermion compounds [12, 13].

Below T_c, the average precession frequency (inset of Fig. 2) is seen to increase continuously down to $T \to 0$ for both values of $B_{\rm TF}$. Since the Knight shift is negative, this implies a decrease of its absolute value. In the mixed state, a possible additional shift ($K_{\rm d}$) due to the demagnetization and Lorentz fields would reduce the local field at the muon site. Therefore, it cannot account for an increase of $\nu_{\rm tot}$ 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 $T_{\rm c}$ [24].

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 $\Delta_0 \approx 1.76 k_{\rm B} T_{\rm c}$) [14, 15]. The decrease of the SC carrier density due to the increase of $B_{\rm TF}$ is directly observed through a non-zero shift at $T \to 0$. 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 [16]. The strong electron-phonon coupling and the dirty limit cases (the latter being unlikely from the magnetization data) [17] are also presented in Fig. 2. Their steeper variation below $T_{\rm c}$ clearly does not agree with the data.

The T-dependence of $\sigma_{\rm Ga}$ is presented in the inset of Fig. 3. The reduction of $T_{\rm c}$ and an increase of the internal field homogeneity (i.e., a decrease of $\sigma_{\rm Ga}$), is clearly observed when $B_{\rm TF}$ is increased. In the extensively studied cuprates and heavy fermions, the conditions $\kappa \gg 1$ and $B_{\rm TF} \ll B_{\rm c2}$ imply that the ratio $\sigma_{\rm Ga}/\lambda^{-2}$ is roughly T- and $B_{\rm TF}$-independent [6, 7]. Here, the artificial reduction of $\sigma_{\rm Ga}$ due to the overlap of the vortices near $B_{\rm c2}$ 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 $B_{\rm c2}(T)$ [5]. Calling this quantity $f(b)$, the function $\lambda^{-2} \propto f(b)\sigma_{\rm Ga}$ 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 [14, 15], and as shown by the fit with weak electron-phonon coupling in the clean limit (Fig. 3) [25].

We finally discuss the field dependence of $\sigma_{\rm Ga}$ at low-T. We measured $\sigma_{\rm Ga}$ 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 $B_{TF} > B_{\rm c2}$. The results of the fits with Eq. 1 are presented in Fig. 4. For small fields ($B_{\rm TF} \lesssim B_{\rm c1}$), $\sigma_{\rm Ga}$ continuously increases with $B_{\rm TF}$. A strong inhomogeneity of the electron density of state in Ga_{84}, as well as the powder nature of the sample as suggested in [9], may lead to some FLL bending around SC grains and an inhomogeneity responsible for a non-zero $\sigma_{\rm Ga}$. When $B_{\rm TF} \gtrsim B_{\rm c1}$, $\sigma_{\rm Ga}$ reflects both the FLL organization [5] and the field dependence of λ^{-2}. For high fields ($B_{\rm TF} \gtrsim B_{\rm c2} \sim 0.2$ T at 2 K), the superconductivity is destroyed and an homogeneous field ($\sigma_{Ga} = 0$) is recovered. The ratio $\lambda/\lambda(0) \propto [f(b)\sigma_{\rm Ga}]^{-2}$

is presented in 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 [18], 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, 19]. 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 field distribution, as seen by the usual [9, 20] reduction of $\sigma_{\rm Ga}$ in the FC case (which also reduces the sensitivity of the experiment). However, the shape of the variation does not seem to be changed.

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 (three 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 [21], 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. 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.

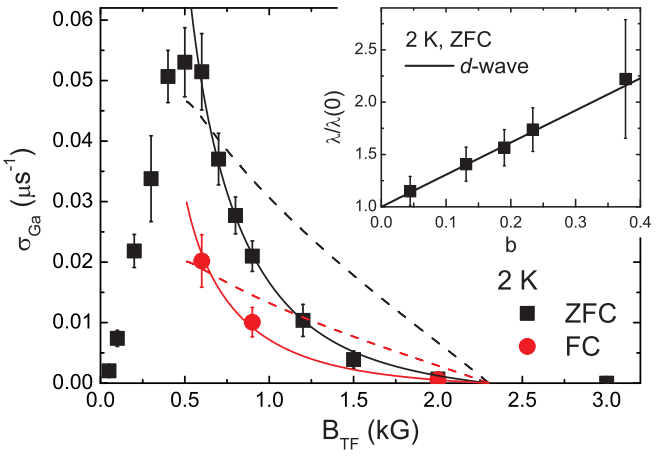

FIG. 4: $H_{\rm TF}$-dependence of $\sigma_{\rm Ga}$, in ZFC and FC conditions. The pinning accounts for the difference. Inset: $\lambda(b)/\lambda(0)$. The lines are computations with $\kappa = 2$, a constant λ (s-wave, dashed lines) and $\lambda/\lambda(0) \propto 1 + 3.1(5)b$ (d-wave, solid lines).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

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[22] The Al used is comparable to the "pure" one of [8].
[23] Notice that there is *a priori* no reason to find $K_{\mathrm{Ga,n}} \sim K_{\mathrm{bgd}}$, a relationship which is clear, however, from the narrow resonance line measured at high-T.
[24] Since the local field at the muon site is involved, the demagnetizing and Lorentz field would cancel for perfectly spherical superconducting particles. For approximately spherical crystallites, as in our powder sample, the resulting correction is therefore quite small. Demagnetizing corrections arising from the shape of the sample holder are likewise small, since it was a very flat disk and the transverse field was parallel to the platelet.
[25] Quantitatively, the value $1/\sqrt{f(b)\sigma_{\mathrm{Ga}}(0)} \sim 1000$ nm is one order of magnitude larger than λ evaluated from the magnetization data. This may be due to both the non-Gaussian fit and the non ideal GL triangular FLL case.