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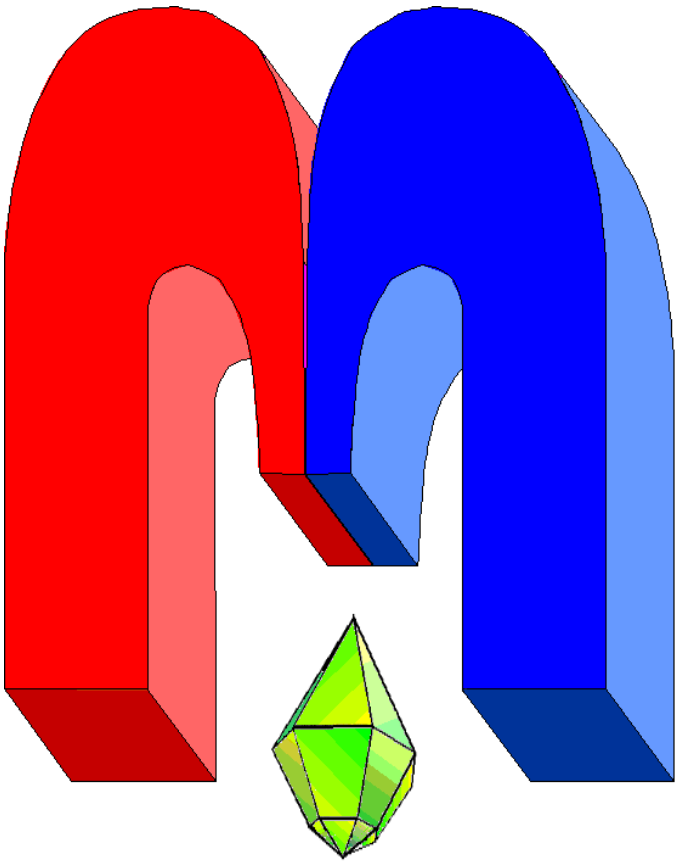

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Disorder effect and the vortex phase transition in layered organic superconductor κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br

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We report systematic detailed measurement of the superconducting properties on the layered organic superconductor κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br near 80 K and the effect of disorder on the superconducting transition temperature T_c. The reversible part of the magnetization (reversible magnetization) and the magnetic entropy change (ΔS) were studied. Using the London model, we determine the temperature dependence of the London penetration depth (λ) from the slope of the linear $M(\ln H)$ dependence of the isothermal magnetization. Our results show the strong dependence of ΔS and λ on the temperature. The structural transformation which occurs at the vicinity of 80 K very strongly influences the physics of vortex lattice and the associated magnetic behavior.

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Keywords: Organic superconductor, reversible magnetization, magnetic entropy change, vortex pinning, London penetration depth.

Introduction

Organic superconductors exhibit many interesting phenomena, including low dimensionality, strong electron-electron and electron-phonon interactions, the proximity of antiferromagnetism, insulator states and superconductivity [1]. The quasi-two-dimensional molecular series κ-(BEDT-TTF)$_2$X exemplifies the complex interplay of collective phenomena that occur in correlated electron systems [2, 3]. In particular, the proximity of superconducting κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br to a Mott transition, along with possible pseudogap physics and molecular disorder effects, led to the fact that this compound was actively studied [4-8].

The crystal structure consists of alternating layers of conducting BEDT-TTF and insulating X anions, similar to high-T_c materials. Consequently, these superconductors have similar SC properties including the intrinsic Josephson effect [9]. This similarity suggests the existence of the vortex phase transition in the organic layered superconductors as observed in high-T_c superconductors such as $YBa_2Cu_3O_{7-\delta}$. As the temperature scale is much lower in organic materials, the thermal fluctuations are expected to be small compared to the high-T_c compounds. Thus, the comparison between the two types of superconductors can give important clues such as the nature of vortex phase transitions.

A remarkable feature of the electronic state of κ-(BEDT-TTF)$_2$X compound is that, the native quarter filled band is modified to the effective half filled band by the strong dimer structure consisting of two BEDT-TTF molecules [10]. In fact, the BEDT-TTF molecule has two ethylene groups at the end; the two-dimensional conduction planes consist of BEDT-TTF molecular dimers, which form an anisotropic triangular lattice. When the terminal ethylene groups in each BEDT-TTF molecule contain all possible eight hydrogen atoms (H_8), the material shows bulk superconductivity. Upon replacing the hydrogen by deuterium (D_8), T_c greatly reduced, the phase transition becomes broader, and that implies inhomogeneous nature of the superconductivity.

Influence of the cooling rate V_c (velocity of cooling) on the superconducting transition temperature T_c of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br was found in one of the first investigations after synthesis of the compound [11]. Recently this effect has been the subject of numerous studies in the salt with both usual H_8-BEDT-TTF and deuterium substituted D_8-BEDT-TTF molecules (which we will subsequently abbreviate as κ-H_8-Br and κ-D_8-Br salts, respectively). The effect is related to the phase transition at 80 K, due to the order-disorder transformation of the terminal ethylene groups of the BEDT-TTF molecules [12]. The ordering is in fact realized through a sequence of phase transformations in approximately the 60 to 90 K range [13]. Furthermore, organic superconductors exhibit other typical features like the structural transformation around 80 K that can considerably influence the physics of their vortex lattices and the associated magnetic behaviors [14].

Synthesizing partial deuterated molecules of the ethylene groups gives an effective method to see the variation of electronic structure in the metallic region near the boundary region [15]. In κ-D_8-Br salt the transformation leads to a coexistence of two phases, assigned to magnetically ordered insulator and metal [16], suggesting its importance for the band structure.

We have just noticed that the investigation of nuclear magnetic resonance (NMR) has emerged as a vital technique for investigating strongly correlated electron systems, and is particularly important for studying the vortex lattices and phenomena associated with unconventional pairing symmetries.

Since NMR is sensitive to the density of states and is a microscopic probe, it is an ideal technique for investigating the nature of localized impurity states in superconductors and correlated electron systems [17]. Nevertheless, NMR has the potential and versatility to shed important light on the physics of these systems, as well as other classes of materials that may be discovered in the future. In particular, the interplay between antiferromagnetism and superconductivity in different classes of materials and how these order parameters emerge for different classes of quantum critical behavior remain a fascinating area of research.

Joseph Gezo et al. have shown that proton NMR measurements on the organic superconductor κ-(ET)$_2$Cu[N(CN)$_2$]Br exhibit stretched exponential spin-lattice relaxation below $T \approx 25$ K, suggestive of an inhomogeneous magnetic phase that develops in the normal state and coexists with superconductivity [18].

It has been known that strong electron correlations play an important role on the anomalous superconducting properties, such as existence of an antiferromagnetic phase next to the superconductivity [19]. This is presumably reminiscent of unconventional superconductivity in high-T_c cuprates, in which a *d*-wave symmetry of the order parameter has been widely accepted. However, in organic superconductors, although many efforts have been achieved and its unconventional (*d*-wave) symmetry may be predominantly accepted, no clear consensus has been reached yet [20].

We have systematically studied the critical current density (J_c) and the irreversibility line $H_{irr}(T)$ as a function of the cooling rate through the order-disorder transformation near 80 K for the deuterated organic superconductor (κ-D_8-Br). The field and temperature dependences of the critical current density (J_c) were determined, using the Bean's model, from the irreversible parts of the magnetization curves. Our results show the strong dependence of $H_{irr}(T)$ and J_c on the cooling rate [21].

In this work, we report studies of the effect of the cooling rate on the interlayer transports properties at T_c and on the magnetic susceptibility. By freezing the sample into different disordered states, we found that there is a strong evidence for a structural transformation occurring around 80 K. The results of the reversible magnetization and the magnetic entropy change for the κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br sample are also present as a function of temperature at different magnetic fields applied parallel to the crystallographic *b* axis (perpendicular to the layers). In the superconducting state, using the London model, we determine the temperature dependence of the London penetration depth (λ) from the slope of the linear $M(\ln H)$ dependence of the isothermal reversible magnetization.

Materials and Methods

Single crystals of the κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br superconductor were synthesized at the Jean Rouxel Institute of Materials (Nantes, France). Both hydrogenated and deuterated compounds were used in this study. The two samples have an average dimensions: $0.7\times0.7\times0.2$ mm^3 and $1\times1\times0.25$ mm^3,

respectively. Our samples had good magnetic quality and were stable; the results remained unchanged despite repeating the experiment several times. The block-like crystals weighing m = 0.59 mg for κ-H_8-Br and m = 2.07 mg for κ-D_8-Br. Before starting each measurement, the sample was first warmed to a given temperature well above T_c. Once the residual field is eliminated, the sample was zero field cooled (ZFC) or field cooled (FC) to a desired temperature. Magnetic measurements were done with a commercial SQUID based magnetometer (MPMS 5XL SQUID), which produces a magnetic field up to 5 T. Magnetic field was applied perpendicular to the conducting layers. The remnant field at the place of the sample was less than 1 μT.

We have investigated the magnetic susceptibility of the SC phase as a function of the cooling rate in the ZFC conditions. In the slow cooling rate, the sample was cooled from 160-90 K at a cooling rate of about 2 K/min and then from 90-70 K, at a cooling rate of 0.1 K/min. Furthermore, the sample is then kept at the temperature of 70 K during 20 h and then cooled directly to 2 K at a cooling rate of 5 K/min. In the rapid cooling condition, the sample was submerged directly in the variable temperature insert at a temperature of the order of 2 K.

Results and Discussion

To determine the superconducting transition temperature (T_c), we have systematically studied the dc susceptibility under magnetic field H of 5 Oe. T_c is defined as the intercept of the extrapolation of the normal and superconducting states.

Fig. 1 shows the temperature dependence of the magnetic susceptibility of both hydrogenated (κ-H_8-Br) and deuterated (κ-D_8-Br) samples after slow and rapid cooling rate at magnetic field of 5 Oe applied perpendicular to the conducting layers. The superconducting critical temperature (T_c) shifts lower with increasing cooling rate, as can be seen in (Fig. 1), the onset of superconductivity occurs at T_c = 11.7 K in the case of slow cooling and T_c = 10.3 K when the sample was cooled rapidly for the hydrogenated (κ-H_8-Br) sample. By the rapid cooling, the onset decreases to T_c = 10.1 K for the deuterated (κ-D_8-Br) sample, as seen in the inset. The T_c as well as the width of this transition depends on V_c. The cooling-rate dependence of T_c for the κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br salt is consistent with several references [22].

In comparison with the nondeuterated compound, the effect is more pronounced in the case of deuterated (κ-D_8-Br) sample and a much higher sensitivity to cooling are found for this latter. Kawamoto et al. reported that rapid cooling through 80 K drives the SC phase into a disordered magnetic phase in the deuterated κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br compound [23]. This has been interpreted as a strong indication for (κ-D_8-Br) being located right at the border between a SC and a Mott-insulating phase [24, 25]. Rapid cooling through 80 K suppresses the SC phase and increases the magnetic phase [26]. The presence of a disorder of anions in these materials influences the properties of the SC phase and quite particularly the physics of the vortex lattice pinning.

The magnetization vs magnetic field (*M-H*) curves exhibit typical type-II superconducting behavior. The Fig. 2 shows typical results for the initial magnetization curves for deuterated (κ-D_8-Br), obtained at several temperatures, with **H** perpendicular to the conducting layers to the film, after slow cooling rate. One can see that the magnetization increases with increasing temperature and magnetic field.

At the higher temperatures, M versus H exhibits decrease curvatures which progressively decrease as the temperature decreases. For values of the magnetic field larger than 300 Oe, M may be assumed linear in H. According to thermodynamical theory [27], the isothermal magnetic entropy change associated with a magnetic field variation is given by:

$$\Delta S_M(T,\Delta H) = S_M(T,H) - S_M(T,0) = \int_0^{H_M} \left(\frac{\partial S(H,T)}{\partial H}\right)_T dH. \quad (1)$$

From the Maxwell's thermodynamic relation:

$$\left(\frac{\partial S(H,T)}{\partial H}\right)_T = \left(\frac{\partial M(H,T)}{\partial T}\right)_H, \quad (2)$$

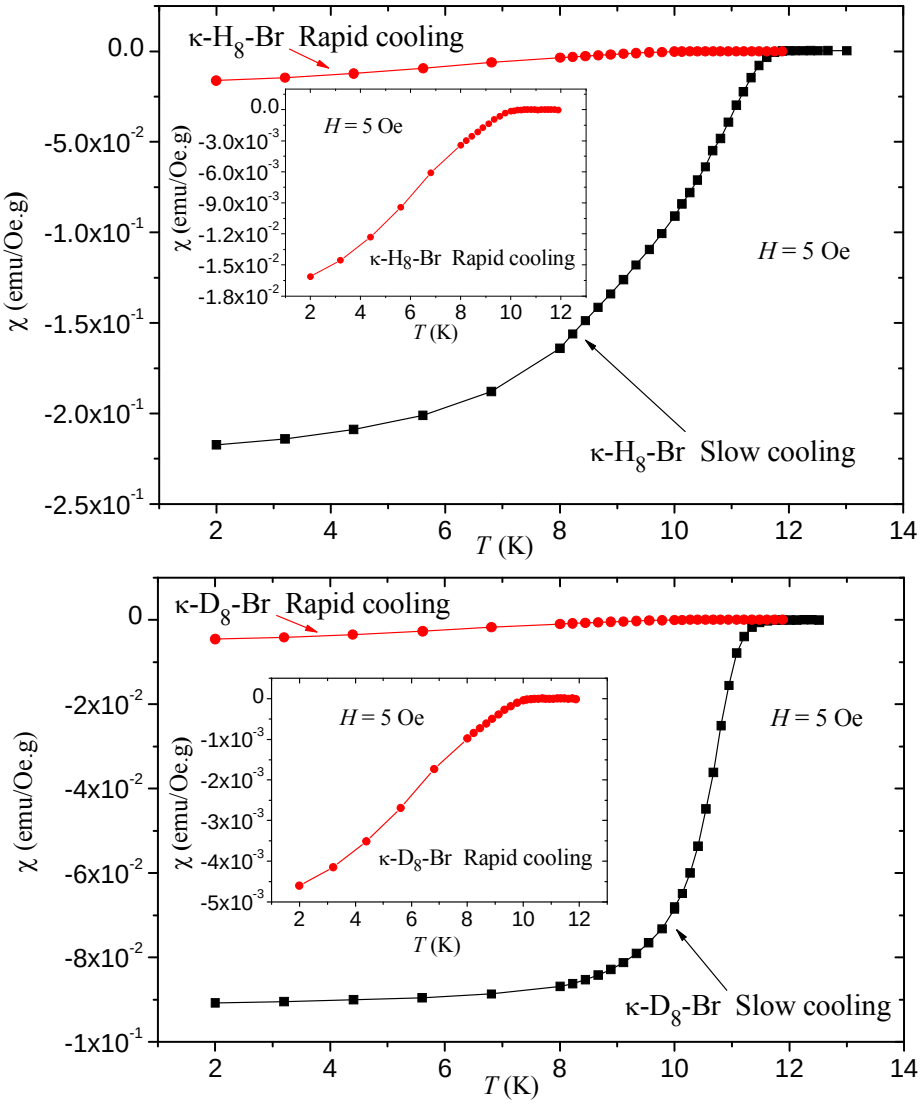

Figure 1. Temperature dependence of the magnetic susceptibility at magnetic field $H = 5$ Oe for both hydrogenated (κ-H_8-Br) and deuterated (κ-D_8-Br) samples in slow and rapid cooling. The results after rapid cooling are expanded in the insets for two samples.

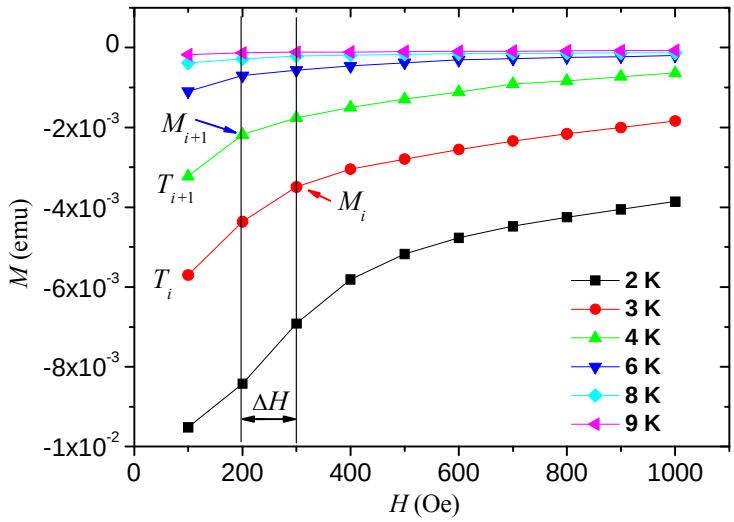

Figure 2. Magnetic isothermals with increasing field at some selected temperatures for deuterated (κ-D_8-Br) in slow cooling rate.

we can get the following expression:

$$\Delta S_M\left(T,\Delta H\right)=\int_0^{H_{\max}}\left(\frac{\partial M(H,T)}{\partial T}\right)_H dH, \tag{3}$$

where S, M, H, and T are the magnetic entropy, magnetization of the material, applied magnetic field and the temperature of the system, respectively. From the magnetization measurements made at discrete field and temperature intervals, ΔS_M can be approximately calculated by the following expression:

$$\Delta S_M\left(T,\Delta H\right)=\sum_i\frac{M_{i+1}(T_{i+1},H)-M_i(T_i,H)}{T_{i+1}-T_i}\Delta H, \tag{4}$$

where i represents the sequence of experimental measured points and the magnetic field changing by an interval of ΔH = 100 Oe, as presented in Fig. 2.

The resulting temperature dependence of ΔS with the magnetic field of 1 kOe are shown in Fig. 3 for deuterated (κ-D_8-Br). Above 10 K close to T_c , the entropy change increases rapidly with temperature, which is comparable to that of HTSC [28, 29]. However, this divergent dependence near T_c is mainly due to the finite superconducting transition. The presence of a disorder of anions in these materials influences the properties of the SC phase and quite particularly the physics of the vortex lattice pinning. That ΔS is quite sensitive to the disorder of the sample; in the disorder induced sample the entropy change becomes small or the melting transition disappears.

Fig. 4 shows typical isotherms of the magnetization of deuterated (κ-D_8-Br) measured upon increasing fields on a logarithmic field scale.

We turn to deriving the in-plane penetration depth from measurements of the isothermal reversible magnetization curves $M(H)$. Using the interaction energy between vortices and thermodynamic arguments, Kogan et al. [30] developed a theory in the London limit for the vortex state magnetization of a uniaxial, high - κ type II superconductor. In particular, the reversible magnetization for intermediate fields $H_{C1} \ll H \ll H_{C2}$ (H_{C1} and H_{C2} are the lower and upper critical fields, respectively) is given by London's phenomenological model [31],

$$M=-\left(\frac{\phi_0}{32\pi^2\lambda^2}\right)\ln\left(\frac{\beta H_{C2}}{H}\right), \tag{5}$$

where $\phi_0 = 2.068\ 10^{-7}$ (G·cm^2) is the magnetic flux quantum, $\beta = 0.35$ is a constant and $H_{C2}(T)$ is the upper critical field corresponding to the applied field direction.

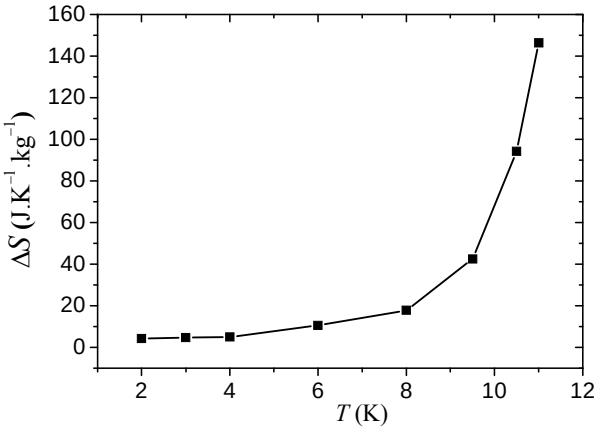

Figure 3. Temperature dependence of magnetic entropy change under a magnetic field of 1 kOe (zero field cooling process) for deuterated (κ-D_8-Br) after slow cooling rate.

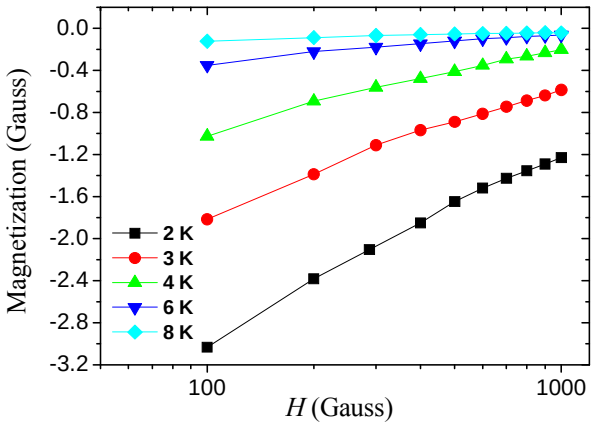

Figure 4. Isothermal magnetization curves vs ln H plots in κ-D_8-Br at different temperatures in the slow-cooled condition. A factor of 318.3 was used to transform in units of Gauss.

The deviation of isothermal magnetization from the logarithmic field dependence expected in the London regime including the vortex-fluctuation term. This may reflect the presence of interactions between the vortices. We have noticed that including the fluctuation of vortices in the original London approach is not sufficient to explain the behavior of the reversible magnetization of the quasi two-dimensional oxide superconductors.

A generalization of the above isotropic model to the anisotropic uniaxial case has been obtained by introducing an effective mass tensor [30]. According to this work, the slope of the linear $M(\ln H)$ dependence is given by:

$$\frac{dM}{d(\ln H)} = \frac{\phi_0}{32\pi^2\lambda^2}. \tag{6}$$

Fig. 5 shows typical slop $dM/d(\ln H)$ (which is expected to be directly proportional to $1/\lambda^2$) and in-plane magnetic penetration depth as a function of the temperature of deuterated (κ-D_8-Br). In the slow-cooled state, the number of ethylene disorders will be small and thus it is fruitful to compare with the London penetration depth λ.

The variation of $\lambda(T)$ at low temperature suggests the existence of gapless excitations. The similarities between these materials and the cuprates suggest that these excitations may originate from a d-wave pairing state. In a pure *d*-wave superconductor it is well established that $\lambda_{in\text{-}plane}$ will vary linearly with T at the lowest temperatures.

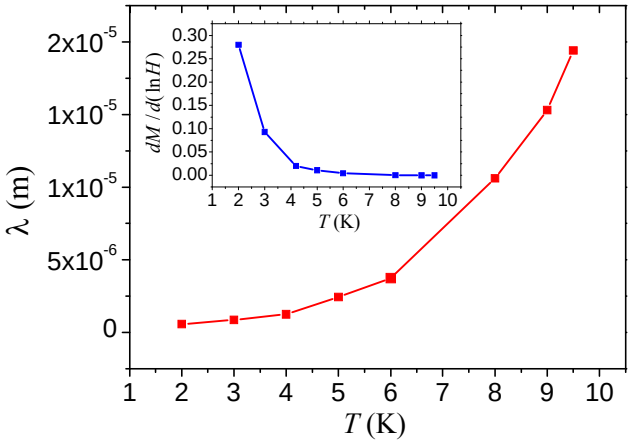

Figure 5. In-plane magnetic penetration depth as a function of the temperature of deuterated κ-D_8-Br after slow cooling condition. The inset is a plot of the slop $dM/d(\ln H)$ versus temperature.

Summary

In conclusion, we reported the magnetic susceptibility and the reversible magnetization measurements to investigate the disorder effect and the vortex phase transition in organic superconductor κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br. Our results show that magnetic entropy change depends strongly on the temperature. The cooling rate has a considerable effect on the superconducting properties; the effect is much less in the case of hydrogenated salts. In particular, the cooling rate near 80 K controls the amount of disorder at low temperature. The SC transition temperature T_c is determined using the dc magnetic susceptibility.

We have found that the SC transition temperature T_c is reduced by rapid cooling through 80 K. We have pointed out that the study of both the transition temperature and the penetration depth in the low temperature limit can give some insight into the pairing mechanism.

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