Muon-spin-rotation study of the superconducting properties of Mo_3Sb_7

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We present the microscopic properties of superconducting state in Mo_3Sb_7 (T_c=2.2 K) using muon-spin rotation measurements. The zero-field-cooled and field-cooled (FC) data with an applied transverse field of 40 mT reveal an irreversibility in the muon relaxation rates and precessional frequencies below 2 K. We have also found an anomaly around 0.5 K, which may be related to a process of the vortex melting or some change in vortex-lattice symmetry. The temperature dependence of FC muon relaxation rate can be analyzed using a phenomenological double-gap *s*-wave model. The observation of a nonlinear field dependence of the muon relaxation rate is consistent with the occurrence of two superconducting gaps. Moreover, the magnetic penetration depth λ, coherence length ξ, superconducting carrier density n_s, and effective-mass enhancement m^* have been found to be $\lambda \approx 665$ nm, $\xi \approx 12.5$ nm, $n_s \approx 1.2 \times 10^{27}$ carriers/m^3, and $m^* \approx 18.7 m_e$, respectively.

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The superconductivity in Mo_3Sb_7 was discovered several years ago,[1] but pairing mechanism in this compound is still under discussion. The conventional BCS-type mechanism was first proposed based on the magnetization data.[1] On the other hand Dmitriev *et al.*,[2] using point-contact (PC) Andreev-reflection data, have suggested either a $(s+g)$ wave or another unconventional mechanism. Furthermore, Candolfi *et al.*[3] have reported magnetic susceptibility, specific heat, and electrical resistivity down to 0.6 K and have interpreted their data within the framework of the spin-fluctuation theory. Thus the mechanism of superconductivity and nature of pairing wave function in Mo_3Sb_7 is an open debate. Therefore, recently we have also measured specific heat down to 0.4 K and in magnetic fields up to 2.5 T. Interestingly, our data hint the presence of two BCS-type gaps with $2\Delta(0)_1 = 4.0 k_B T_c$ and $2\Delta(0)_2 = 2.5 k_B T_c$.[4] The multigap scenario seems to be supported by field dependence of the Sommerfeld ratio C_p/T at 0.4 K, where one recognizes a nonlinear $C_p(H)/T$ dependence. Since, the PC Andreev reflection and specific-heat measurements have not given pairing mechanism unambiguously, the precise technique, such as muon-spin rotation (μSR) would be helpful in this matter. The muon-spin depolarization function which, in the case of a type-II superconductor, results from the distribution of local fields in the vortex state. This depolarization, or more precisely the Fourier transform, can provide unique and detailed insights into flux distribution and hence into the nature of the flux-line lattice, flux lattice melting, and flux pinning. The second moment of the internal field distribution in a type-II superconductor is a function of the penetration depth λ, the coherence length ξ, and the temperature dependence is a measure of the superconducting gap. Indeed, μSR has been used to show the existence of multiple gaps in MgB_2,[5] $La_{1.83}Sr_{0.17}CuO_4$,[6] La_2C_3, and Y_2C_3.[7]

In this paper, we report on measurements of the muon-spin rotation for Mo_3Sb_7 in the superconducting state. As we show below, different dynamics of motion of flux-line lattice in Mo_3Sb_7 is clearly visible in the zero-field-cooled (ZFC) and field-cooled (FC) measurements. In addition to the irreversibility temperature (about 2 K for $\mu_0 H$=40 mT), the temperature dependency of the muon depolarization rate and muon-spin precessional frequency exhibits an anomaly near 0.5 K, which can be interpreted due to a process of the vortex melting or some change in vortex-lattice symmetry. The most important result of our studies is also the observation of characteristic temperature dependence of the muon relaxation rate and its field dependence, being described by a phenomenological double-gap *s*-wave model. We also derive the superconducting carrier density 1.2×10^{27} carriers/m^3 and effective-mass enhancement of $18.7 m_e$. The obtained parameters, accompanied with high-temperature transition found at 50 K,[8] could make Mo_3Sb_7 to be a unique example of the bridge between two classes of multiple-transition superconductors: HTc and heavy-fermion ones.

Mo_3Sb_7 was prepared from Mo and Sb powders (purity 99.95% from Alfa Aesar) by solid-state reaction. The procedure of the sample synthesis was described in detail in Ref. 9. Characterization by a scanning electron microscope, energy dispersive x-ray spectrometry, and powder x-ray diffraction indicated that the investigated sample is high-quality single phase of correct stoichiometry. For μSR measurements, pulverized sample of Mo_3Sb_7 (5 g) was mixed with GE-7031 varnish and glued onto a high-purity silver (>4 N) holder of 30 mm diameter and 1 mm thick.

The μSR measurements were carried out using MuSR spectrometer installed at ISIS facility of the Rutherford Appleton Laboratory (Chilton, U.K.). The measurements were performed in transverse field (TF) geometry with applied magnetic fields up to 50 mT and over the temperature range 0.1–2.5 K using ^{3}He-^{4}He dilution refrigerator. Each detector is normalized for the muon decay and rotated into real and imaginary components. These two spectra were simultaneously fitted with a sinusoidal oscillating function with the relaxation Gaussian component $G_z(t) = \Sigma_{i=1}^{2} A_i \exp(-\frac{\sigma_i^2 t^2}{2}) \cos(2\pi \nu_i t + \varphi_{i,\mathrm{real,imag}})$, where the *i*-th component denotes the contribution from the superconducting and background phases, respectively, A_i is the initial asymmetry, σ_i is

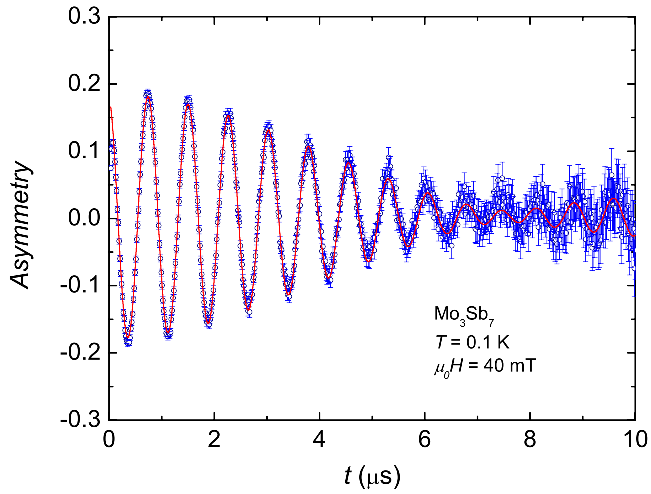

FIG. 1. (Color online) Transverse-field μSR spin precession signals of Mo_3Sb_7 at 0.1 K obtained at an applied field of 40 mT. The solid line represents a least-squares fit of the function described in the text.

the Gaussian relaxation rate, ν_i is the muon-spin precessional frequency, and φ_i is the phase offset. The background term comes from those muons which were implanted into the silver sample holder and therefore this oscillating term has no depolarization, i.e., $\sigma_2=0.0$ μs^{-1}. Typical TF μSR spin precession signals in the superconducting state at applied field of 40 mT are shown in Fig. 1. One notices that μSR measurements were also performed in longitudinal geometry. It appears that there was no change in the relaxations above and below the superconducting transition, thus, this may rule out triplet pairing.

Figure 2(a) shows the muon Gaussian depolarization rate $\sigma(T)$ measured in a transverse field of 40 mT through two different modes: zero-field-cooled and sample field cooled from 2.5 K. The overall behavior of ZFC and FC $\sigma(T)$ of Mo_3Sb_7 resembles very much those of multigap superconductors La_2C_3 and Y_2C_3, respectively.[7] For Mo_3Sb_7 $\sigma(T)$ above T_c is essentially independent of temperature and at 2.5 K amounts to 0.117 μs^{-1}. The temperature independent $\sigma(T)$ in the normal state is usually attributed the relaxation of static, on the time scale of the muon, nuclear moments. Below ~2.2 K, significant increase in $\sigma(T)$ in both FC and ZFC modes is observed. This temperature dependence of $\sigma(T)$ shows the establishment of a flux-line lattice and indeed indicates a decrease of the magnetic penetration depth with decreasing temperature. Comparing of the ZFC and FC data reveals a substantial difference between these data. In the ZFC mode $\sigma(T)$ increases with decreasing temperature faster than that of FC, thus points to difference in the numbers of the pinning sites and trapping energies, altered by magnetic fields and sample history. We may estimate the difference of the width of the local magnetic-field distribution at the muon sites ΔW_H via the calculation of the difference $\Delta W_H=(\sigma_{ZFC}-\sigma_{FC})/\gamma_\mu$, where $\gamma_\mu=135.5$ MHz T^{-1}. The resulting ΔW_H displayed in the inset of Fig. 2(a) suggests an unusual behavior of motion of flux vortices with changing temperature. From the $\Delta W_H(T)$ dependence one detects the irreversibility temperature T_{ir} of about 2 K, which is smaller than T_c. Interesting feature of the ΔW_H data is the appearance of an upturn in ΔW_H below $T_{vm}\approx 0.5$ K. The behavior reflects a sudden rearrangement of flux vortices. Such enhanced ΔW_H could be related to the presence of new trapping energy. A similar two-stage transition of the vortex in superconducting $Bi_2Sr_2CaCu_2O_{8+\delta}$ had been observed by Blasius *et al.*[10] The authors interpreted it as the intraplanar melting of the vortex structure into a liquid phase of flux lines.

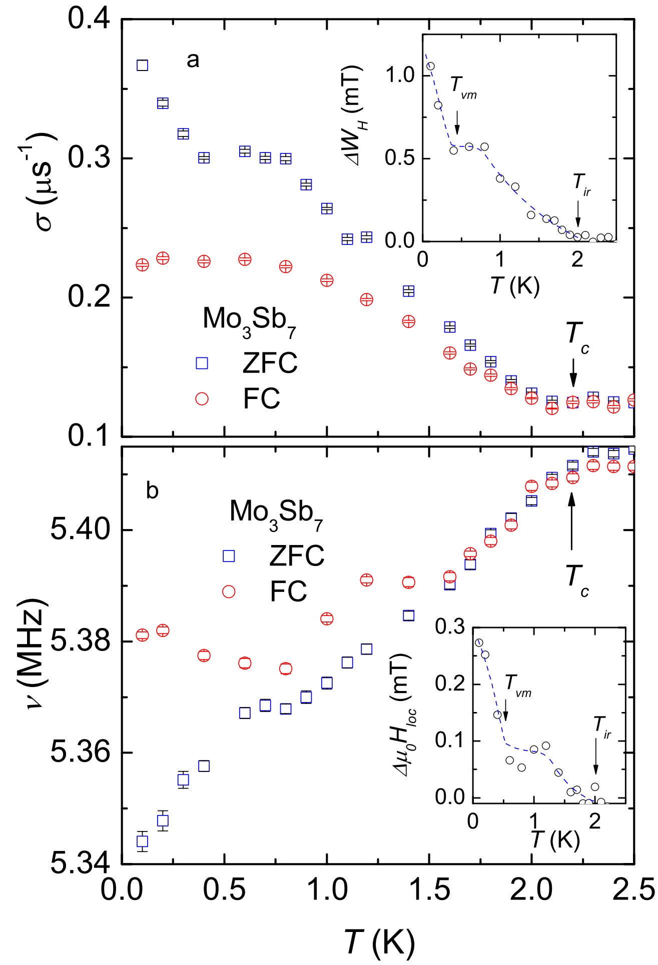

FIG. 2. (Color online) (a) Muon Gaussian depolarization rate in Mo_3Sb_7 taken at a transverse field of 40 mT as a function of temperature. Inset shows temperature dependence of difference of the width of the local magnetic-field distribution at the muon sites measured in ZFC and FC modes. The dashed line is guide for the eyes. (b) Muon-spin precessional frequency in Mo_3Sb_7 measured at a transverse field of 40 mT vs temperature. Inset shows the temperature dependence of difference of local fields sensed by muons in ZFC and FC modes.

The temperature dependence of the muon-spin precessional frequency ν of Mo_3Sb_7 at 40 mT is displayed in Fig. 2(b). In the normal state the value of the muon frequency is about 5.41 MHz, corresponding to a local field of 39.9 mT, practically the same value of the applied field strength. With decreasing temperature below T_c the frequency decreases as a result of the presence of flux lines. At 0.1 K, the ν value in the ZFC mode amounts to 5.34 MHz, i.e., ~39.4 mT. This means that only a small change in the internal field was experienced by muons, which may indicate a minor change

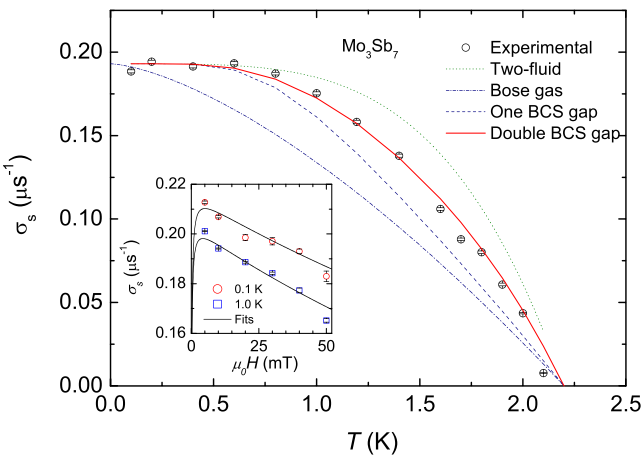

FIG. 3. (Color online) Temperature dependence of the relaxation rate of superconducting phase in Mo_3Sb_7. The dotted, dashed-dotted, dashed, and solid lines are theoretical ones. Inset shows field dependence of σ_s at 0.1 and 1 K. The solid lines are theoretical lines.

in flux-line lattice. Inspection of Fig. 2(b) indicates a distinct effect of irreversibility as observed in the case of $\sigma(T)$ data. We calculated the difference of the fields in the ZFC and FC measurements through the relation $\Delta\mu_0 H_{\mathrm{loc}}=(\nu_{\mathrm{FC}}-\nu_{\mathrm{ZFC}})/\gamma_\mu$ and have shown the temperature dependence of $\Delta\mu_0 H_{\mathrm{loc}}(T)$ in the inset of Fig. 2(b). The obtained $\Delta\mu_0 H_{\mathrm{loc}}(T)$ curve implies different dynamics of the flux vortices motions in the ZFC and FC modes. Again, we observe a steplike enhancement of $\Delta\mu_0 H$ below $T_{\mathrm{vm}}\sim 0.5$ K, indicative of the development of a sudden inhomogeneity of the local fields in the ZFC modes. The irreversibility temperature of 2 K is found also in $\Delta\mu_0 H_{\mathrm{loc}}(T)$ curve.

In order to study the mechanism of electron pairing in Mo_3Sb_7 one must first estimate the relaxation rate associated with nonuniform field distribution of superconducting phase σ_s. We evaluated σ_s from the relation $\sigma_s=\sqrt{\sigma^2-\sigma_n^2}$ (Fig. 3), where σ and σ_n are the relaxation rates obtained in the superconducting and normal states, respectively. To minimize flux pinning we used the relaxation rates in the FC measurements. In the flux-line lattice (FLL) state, σ_s in a conventional superconductor is expected to increase with decreasing temperature according to the empirical relation $\sigma_s(T)=\sigma_s(0)[1-(T/T_c)^n]$. In the two-fluid model, the exponent n would take value of 4,[11] but in model of the ideal charged Bose gas n would amount to 3/2.[12] Using a value of $\sigma_s(0)=0.193$ $\mu\mathrm{m}^{-1}$, we have calculated $\sigma_s(T)$ and plotted as dotted and dashed-dotted lines in Fig. 3, respectively, for the two-fluid and Bose gas models. Clearly, the reproducibility of the data cannot be accepted.

Next, we have analyzed the $\sigma(T)$ dependence using the approach[5] $\sigma_s(T)=\sigma_s(0)-\delta\sigma(\Delta,T)$, where

$$\delta\sigma(\Delta,T)=\int_0^\infty f(\epsilon,T)[1-f(\varepsilon,T)]d\epsilon,$$

$$f(\epsilon,T)=\{1+\exp[\sqrt{\epsilon^2+\Delta(T)^2}/k_BT]\}^{-1},$$

k_B is the Boltzmann constant, and $\Delta(T)$ is temperature dependence of the gap. Following Carrington and Manzano,[13] we used approximated formula $\Delta(T)=\Delta(0)\tanh\{1.82*[1.018*(T_c/T-1)]^{0.51}\}$ with $\Delta(0)$ being the isotropic superconducting gap at 0 T. In Fig. 3 we show theoretical curve (dashed line) obtained with $2\Delta(0)/k_BT_c=3.53$. Apparently, the large difference between experimental and theoretical data provides no support to a conventional single gap s-wave BCS scenario. Finally, a satisfactory fit of the experimental data would be achieved in the fitting to a phenomenological two-gap model $\sigma_s(T)=\sigma_s(0)-w\,\delta\sigma(\Delta_1,T)-(1-w)\,\delta\sigma(\Delta_2,T)$. In fact, the model was proposed by Wang *et al.*[14] and by Bouquet *et al.*[15] some years ago for MgB_2 and was applied for the specific-heat data of Mo_3Sb_7.[4] Following Bouquet *et al.*,[15] the penetration gap below T_c can be considered as the sum of the contributions of two bands characterized by respective gap widths $\Delta_1(T)$ and $\Delta_2(T)$ and by relative weight w. The fitting result is shown in Fig. 3 as the solid line with $2\Delta(0)_1/k_BT_c=4.54$, $\Delta(0)_2/k_BT_c=2.73$, and the weight $w=0.7$. The obtained parameters are quite comparable with the specific-heat data.[4]

From the field dependence of muon relaxation rate we evaluated magnetic penetration depth λ, coherence length ξ, and upper critical field using the modified London equation[16]

$$\sigma_s(H)=\left(\frac{\gamma_\mu}{\sqrt{2}}\right)H\sum_{h,k}\left[\frac{\exp(-\xi^2q_{h,k}^2)}{[1+q_{h,k}^2\lambda^2/(1-H/H_{c2})^2]^2}\right]^{1/2},$$

where $q_{h,k}$ is the lattice sum over the hexagonal FLL. We have fitted the values of $\sigma_s(H)$ at 0.1 and 1 K as shown in the inset of Fig. 3. The best fit (see solid lines) gave $\lambda=665(1)$ nm, $\xi=12.5(9)$, and $\mu_0H_{c2}=2.1$ T for the data at 0.1 K, in good agreement with those from the specific-heat measurements of 660 nm, 12 nm, and 2.24 T. Assuming that the London penetration depth and coefficient of the electronic specific heat are related to the effective carrier mass m^* and the superconducting carrier density n_s as $\lambda_L=(\varepsilon_0 m^*c^2/n_sq^2)^{1/2}$ and $\gamma=\frac{m^*(3\pi^2n_s)^{1/3}k_B^2}{3\hbar^2}$, and taking $\lambda=665$ nm and $\gamma(0.4\ \mathrm{K},2\ \mathrm{T})=42$ mJ $\mathrm{mol_{fu}^{-1}}$ K^{-2} one evaluates $m^*=18.7m_e$ and $n_s=1.19\times10^{27}$ m^{-3}. It is necessary to caution that the magnetic penetration depth would be strongly modified by the presence of impurities and then the estimated m^* and n_s may include some large errors. For example, if 25% overestimation of λ_L, the effective mass and density of charge carriers could change to $16.2m_e$ and 1.84×10^{27} m^{-3}, respectively. On the other hand, if taking the extrapolated to 0 K electronic heat coefficient $\gamma_0=34.5$ mJ $\mathrm{mol_{fu}^{-1}}$ K^{-2} ones gets $m^*=16.1m_e$ and $n_s=1.03\times10^{27}$ m^{-3}. In any case, the values of m^* and n_s observed in Mo_3Sb_7 are comparable to those found in the filled skutterudite $PrRu_4Sb_{12}$ ($m^*\sim10m_e$ and $n_s\sim4\times10^{27}$ carriers/m^3).[17] The $\sigma(H)$ data at 1 K show similar field dependence to those at 0.1 K, and the fit yields $\lambda=704$ nm, $\xi=14$ nm, and $\mu_0H_{c2}=2.1$ T. It is of interest to compare the nonlinear field dependence of σ_s, which was observed for numbers of superconductors, for instance, $PrRu_4Sb_{12}$,[17] $NbSe_2$, $YBa_2Cu_3O_{6.95}$, and $LuNi_2B_2C$.[18] It may recall that $NbSe_2$ is a double-gap superconductor. Thus, our experimental data of C_p and μSR indicate that Mo_3Sb_7 may belong to the family of multigapped compounds such as MgB_2, $La_{1.83}Sr_{0.17}CuO_4$, La_2C_3, and Y_2C_3. The recent calculation of electronic band structure[8] had suggested the Fermi surface to consist of four main bands, in which one distinguishes the heavier band formed by the 4d electrons of the Mo atoms and the lighter band composed by s or p electrons of the Sb atoms. Such large difference in the density of states and resulting in different Fermi velocities between these two bands probably leads to the formation of two superconducting gaps in these two parts of the Fermi surface.

In summary, we have carried out a transverse field muon-spin rotation experiment on the superconductor Mo_3Sb_7 and have determined the muon depolarization rate and precession frequency in ZFC and FC modes. We found a large irreversible effect below irreversibility temperature, which results from the pinning of magnetic-flux vortices. We observed a sudden change in $\sigma(T)$ and $\nu(T)$ at about 0.5 K, probably due to a process of the vortex melting or to some change in the vortex-lattice symmetry. Further work on small-angle neutron scattering (SANS) would help in further understanding the nature of the phase transition near 0.5 K. From the temperature dependence of the muon-spin relaxation we estimated the magnetic penetration depth and coherence length. The $\sigma_s(T)$ dependence is more consistent with the scenario of two distinct BCS-type superconducting gaps with $2\Delta(0)_1/k_BT_c=4.54$ and $\Delta(0)_2/k_BT_c=2.73$. The field dependence of $\sigma_s(H)$ provides strong support for this interpretation. The values of $2\Delta(0)_1/k_BT_c$, $\Delta(0)_2/k_BT_c$, $\lambda=665$ nm, and $\xi=12.5$ nm are in well agreement with those deduced from the specific-heat data. We also derived superconducting density and effective-mass enhancement to be 1.2×10^{27} carriers/m^3 and $18.7m_e$, respectively. The enhanced effective mass m^* and the reduced superconducting carrier n_s, together with the dimer spin gap transition reported previously,[8] could make Mo_3Sb_7 to be an unique candidate of the bridge between two classes of the multiple-transition superconductors: HTc ($m^*\sim3m_e$ and $n_s\sim1\times10^{28}$ carriers/m^3) and heavy-fermion ($m^*\sim100m_e$ and $n_s\sim1\times10^{26}$ carriers/m^3) superconductors.

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