Single-gap superconductivity in Mo$_8$Ga$_{41}$

Z. Pribulová,$^1$ M. Marcin$^1$, J. Kačmarčík,$^1$ M. Kopčík,$^1$ V. Vaňo,$^2$ P. Szabó,$^1$
C. Marcenat,$^3$ V. Yu. Verchenko,$^{4,5}$ A. V. Shevelkov$^4$ and P. Samuely$^1$

$^1$Centre of Low Temperature Physics, Institute of Experimental Physics SAS, Watsonova 47, 040 01 Košice, Slovakia
$^2$Faculty of electrical engineering and informatics, Technical University, Letná 9, SK-04001 Košice, Slovakia
$^3$SPSMS, UMR-E9001, CEA-INAC/UJF-Grenoble 1, 17 Rue des martyrs, 38054 Grenoble, France
$^4$Department of Chemistry, Lomonosov Moscow State University, 119991 Moscow, Russia
$^5$National Institute of Chemical Physics and Biophysics, 12618 Tallinn, Estonia

In the paper, potential two-gap superconductivity in Mo$_8$Ga$_{41}$ is addressed in detail by means of thermodynamic and spectroscopic measurements. Combination of highly sensitive ac-calorimetry and scanning tunneling microscopy (STM), as bulk and surface sensitive probes, utilized on the same piece of crystal reveals that there is only one intrinsic gap in the system featuring strong coupling. Traces of multiple phases seen by STM and also in the heat capacity measured at high magnetic field in a high quality and seemingly single phase crystal might mimic multigap superconductivity suggested in previous papers.

Two-gap superconductivity is a compelling phenomenon and a hunt for its representatives continues since the experimental justification of two energy scales in MgB$_2$ [1] two decades ago. Thereupon, various superconducting materials with unconventional performance were reconsidered in light of these ideas, and new materials are inspected in search for two-gap behaviour as it comprises rich niches of condensed matter physics, including e.g. new mechanism for spontaneous symmetry breaking in systems of superconducting vortices [2], or existence of fractional vortices [3]. Interesting aspects have been intensively studied in iron pnictides and selenides [4].

Two-gap superconductivity was proposed for example in Cu$_4$TiSe$_2$ from muon spin rotation experiments [5] and in β-Bi$_2$Pd from the heat capacity and the upper critical magnetic field behavior [6] but it has been disproved when a combination of highly sensitive techniques was employed in Ref.[7,8]. Thus, multiple-gap superconductivity can be mimicked in some properties just reminding the true inherent multiple order parameters and before any definite conclusion a combination of techniques capable to address several aspects of the phenomenon are needed.

Recently it was suggested that Mo$_8$Ga$_{41}$ features two-gap superconductivity that vanishes upon the vanadium substitution [9]. The material is a member of endohedral gallium cluster compounds. In the structure of Mo$_8$Ga$_{41}$, each Mo atom is placed inside a cage of 10 Ga atoms forming endohedral clusters that share all their vertices. This architecture resembles that of perovskite oxides, among which various important superconductors, including high-$T_c$ oxides, can be found. Recently it was also noted that superconductivity and structural stability probably compete in this family of endohedral gallium cluster superconductors [10]. Therefore, unconventional features in Mo$_8$Ga$_{41}$ might be anticipated. There are several members of this family that are known to be superconducting. Besides Mo$_8$Ga$_{41}$ with $T_c \sim 9.8$ K [11], superconductivity was also reported in Mo$_9$Ga$_{31}$ with $T_c \sim 8$ K [12].

Superconducting properties of Mo$_8$Ga$_{41}$ were studied by transport and thermodynamic measurements in ref. [13]. Heat capacity and magnetic susceptibility were measured on a collection of single crystals glued together in order to obtain reasonable signal. For transport measurements, polycrystalline samples were used. Indications for strong-coupling superconductivity in the system were found. In the subsequent study by means of muon spin rotation/relaxation spectroscopy, it was suggested [9] that two superconducting energy gaps exist in Mo$_8$Ga$_{41}$.

Here we present a comprehensive study of superconductivity in individual single crystals of Mo$_8$Ga$_{41}$ by means of bulk and surface sensitive methods. ac-calorimetry is employed to study fine structure of the heat capacity jump at the superconducting transition by sweeping temperature or magnetic field, while scanning tunneling microscopy and spectroscopy are used to directly probe superconducting gaps. By studying single crystals of Mo$_8$Ga$_{41}$, we aim to clarify possible multigap behavior of this intermetallic superconductor. Crystals were isolated using the flux growth method. Details of synthesis can be found in the previous report [13].

Thermodynamic properties were measured by the ac-calorimetry using a light emitting diode as a contact-less source of heating power. The light was directed towards the sample using an optical fibre [14]. ac-calorimetry is a very sensitive method, which enables registration of relative changes of the heat capacity in single-crystalline samples in the continuous measurement mode. Individual crystals were glued on a chromel-constantan thermocouple, which served both as a sample holder and a thermometer to detect oscillations of the sample temperature. Correction of the Cernox thermometer and the thermocouple in magnetic field were carefully inspected and accounted for during the data treatment. The measured heat capacity includes also addenda, which is the contribution of thermocouple and glue. In order to subtract the addenda from the total heat capacity, the empty thermocouple was measured in zero magnetic field and in fields up to 10 T. In the experiment, the heat was supplied to the sample at a frequency of several Hertz. Measurements were performed down to 0.5 K in $^3$He cryostat in 8 T horizontal, and 10 T vertical magnet.

Tunnelling microscopy and spectroscopy experiments were performed employing a homemade scanning tunnelling microscope (STM) in a commercial Janis SSV cryomagnet system with a $^3$He refrigerator and controlled by the Nan-
FIG. 1: Heat capacity results: a) Upper inset: Photo of the sample mounted on a thermocouple with the optical fibre in the background. Main panel: heat capacity of the sample measured in 0 T and 8 T. Lower inset: field dependent part of the electronic heat capacity from present study (empty symbols, only one out of 50 points is shown for clarity), and from the previous study Ref.[13] (filled blue symbols), the line is a theoretical curve from α model with the coupling ratio $2\Delta/kT_c = 4.4$. b) Heat capacity after normal state contribution subtraction, arrows point to onset of superconductivity. Temperature sweeps measured at 7, 6, 5, 4, 3, 2, 1, 0.5, 0.2, and 0 T, from left to right. Inset: field sweeps of the heat capacity normalized to the normal state contribution measured at 7.15, 5.2, 4.19, 3.17, 2.21, 1.71 K from left to right, curves are shifted on Y-axis for clarity. c) Upper critical field from the heat capacity measurements determined at the mid-point of the anomaly (empty symbols) and at the onset of the transition (filled symbols), from temperature sweeps (squares) and field sweeps (circles). Full lines are theoretical curves from WHH model, green dashed line is a theoretical curve for strong-coupling superconductor taken from Ref.[20].

otechs Dulcinea SPM electronics allowing measurements down to 400 mK in magnetic field up to 8 T. The sample was polished on Al$_2$O$_3$ plate before experiment. A gold STM tip was used, first mechanically cut, then sharpened in situ by controlled collision with bulk gold followed by observing evolution of the tunnelling current with tip-sample separation (d$V$/dz measurement) afterwards. Characteristic series of steps in tunnelling conductance with the final step having the value of the conductance quantum $G_0 = 2e^2/h \approx 77.48 \mu S$ signify an approximately conical tip with a single atom at the end. The spectroscopy measurements were performed by obtaining current-voltage ($I-V$) characteristics, then numerically differentiating the $I-V$ curves to acquire the tunnelling conductance spectra $G(V) = dI(V)/dV$ and normalizing those to the normal state conductance $G_N$. Tunnelling spectra were fitted by the tunnelling conductivity model for the normal metal-superconductor (N-I-S) tunnelling junction [15], with the thermally smeared BCS density of states of the superconducting electrode. The density of states of the gold tip is considered constant in the measured bias voltage range, thus, the spectra directly represent the density of states of the superconducting sample. Two-gap spectra were fitted by the convolution of two BCS conductance spectra only differing in the gap value $\Delta(T)$ with complementary weights ($w_1$ and $w_2 = 1 - w_1$ respectively). The spectral conductance maps were measured at $T = 450$ mK in zero magnetic field using the Current Imaging Tunnelling Spectroscopy technique [16] with 128x128 spatial resolution for a given surface area and using a bias voltage range of ±8 mV.

Bulk properties of the samples were investigated using ac-calorimetry. The main panel of Figure 1a. shows the total heat capacity divided by temperature $C/T$ of the inspected sample measured in 0 T and 8 T magnetic fields, after subtraction of addenda. In zero magnetic field, the anomaly at the superconducting transition is clearly visible at $T_c \approx 10$ K. The anomaly is sharp, indicating good quality of the sample. In the 8 T measurement no clear anomaly is present, however further analysis of the data showed that superconductivity is not fully suppressed in overall temperature range by this magnetic field, there is still some small contribution at low temperatures. In the lower inset of Fig.1a, field dependent part of the electronic heat capacity from this study (empty black symbols), calculated as $\Delta C(T) = C(0T)/T - C(8T)/T$ is plotted. Subtracting the 8 T data removes lattice contribution from the total heat capacity and leaves only the field-dependent electronic part. The inset includes also the data from the previous report [13] calculated in the same way (filled blue symbols). Overlap of the two sets of data is very good except in the limited range at low temperatures. Note that not all of the data points from our recent measurement (black symbols) are shown in the figure, only one point out of 50 is displayed for clarity. The solid black line is a theoretical curve according to the α-model [17], which corresponds to a single-gap superconductor with the coupling ratio of $2\Delta/kT_c = 4.4$. The theoretical line follows the experimental data in very good agreement, except the low-temperature region below 3 K, where the additional contribution to the heat capacity measured in 8 T is present as mentioned above. The value of $2\Delta/kT_c = 4.4$ exceeds the weak coupling limit of the BCS theory, which is $2\Delta/kT_c = 3.5$, indicating strong electron-phonon coupling in
FIG. 2: Tunnelling microscopy and spectroscopy results: a) Surface topography of a 200x200 nm$^2$ surface area at 450 mK; b) Superconducting gap map of the area; c) Tunneling conductance spectra at 3 points of the scanned area marked by the crosses in Fig.2a in matching colors, the curves are shifted for clarity. The dashed lines correspond to zero conductance level. The lines are theoretical fits.; d) Gap temperature dependences (symbols) measured at the positions marked by the crosses in Fig.2a and BCS fits (lines); e) Tunnelling spectra (symbols) measured along the white line in Fig.2a between two well defined phases with characteristic $\Delta(0) = 0.6$ and 1.6 meV, resp. Curves are theoretical fits (lines).

the superconducting state. For illustration, the upper inset of Fig.1a shows a snap-shot of the experimental arrangement - the sample mounted on a thermocouple in front of the optical fibre, which provides light towards the sample to supply heat.

In Figure 1b evolution of the heat capacity with both temperature and magnetic field is shown. Main panel of the figure depicts superconducting anomaly while sweeping the temperature at various fixed magnetic fields. Increasing magnetic field shifts the anomaly towards lower temperatures. At relatively low fields the anomaly remains sharp, but when increased the anomaly broadens and finally at high fields it splits in two. Arrows inserted in the figure are to highlight onset of the transition. Similarly, splitting of the jump at the transition is observed in field-sweep measurements. Inset of Fig.1b shows several heat capacity measurements while sweeping the magnetic field at several fixed temperatures. The curves are normalized to the value in the normal state i.e. above the superconducting transition, and are shifted on Y-axis for clarity. Again, the arrows point to the onset of superconducting transition. Note that at low temperatures (two upper curves) the anomaly reveals two distinct jumps.

Using the temperature- and field-dependent heat capacity data, the upper critical field $\mu_0H_{c2}$ as a function of temperature was constructed (Figure 1c). Empty symbols refer to the mid-point of the anomaly, filled symbols correspond to the onset of superconducting transition marked by arrows in Fig.1b; squares are determined from the temperature sweeps and circles from the field sweeps. Solid lines are predictions according to the Werthamer, Helfand and Hohenberg (WHH) model [18] in the absence of paramagnetic and spin-orbit contributions ($\alpha=0$, $\Delta_w=0$) rescaled by different factors to match the low-temperature saturation of the $\mu_0H_{c2}$ temperature dependence. The $\mu_0H_{c2}(T)$ dependence displayed by empty symbols (at the mid-point of the transition) reveals a pronounced positive curvature and deviates from the WHH theoretical curve above 7 K. The corresponding red WHH curve yields $T_c = 9$ K, which is significantly lower than the value observed in the heat capacity measurements in zero magnetic field. A positive curvature close to $T_c$ of the $\mu_0H_{c2}$ temperature dependence is a usual consequence of the interplay between two gaps [19] and might, at first glance, suggest two-gap behavior also in Mo$_8$Ga$_{41}$. However, splitting of the anomaly at the superconducting transition suggests that several phases with different critical temperatures exist in the sample rather than two distinct gaps with incident $T_c$. Superconductivity in one phase is suppressed more rapidly and some other phase survives to higher fields. Indeed, if $\mu_0H_{c2}$ is determined at the onset of the transition (filled blue symbols in Fig.3), including the second transition, it fits the theoretical WHH curve well. Thus we consider the onset of the transition to be a better criterion for the determination of $\mu_0H_{c2}$ corresponding to the dominant Mo$_8$Ga$_{41}$ phase with the largest gap. Small positive curvature
of $\mu_0H_c^2(T)$ close to $T_c$ might be either connected to the inhomogeneity, or be a consequence of the strong electron-phonon coupling. The latter is supported by the theoretical curve for a strong-coupling superconductivity taken from Ref.[20].

To study local properties of the samples, a surface sensitive scanning tunnelling microscopy/spectroscopy was employed. Surface topography scans reveal inhomogeneous surface morphology consisting of a wide variety of differently shaped and sized regions, usually protruding 10-20 nm from the surface of the sample. This is accompanied by a wide spatial distribution of the energy gap $\Delta(0)$ as evidenced by tunnelling spectra fits, suggesting the presence of several different surface phases. Figure 2 presents the results of a spectral map measurement performed to verify this picture. The surface topography of a 200x200 nm$^2$ area in Fig.2a shows multiple regions, which become clearly distinguished on the gap map in Fig.2b. The values of the superconducting gap $\Delta(0)$ range from 0.3 meV in the protruding area to 1.75 meV in the deepest parts of the valley in the middle of the scan. Fig.2c shows typical spectra of the three main distinct areas of the scan, with their positions marked by the crosses in Fig.2a in the matching colors. The curves in Fig.2c are shifted for clarity, the dashed lines are to visualize zero conductance. The lines are theoretical fits giving the gap values $\Delta(0) = 1.72, 1.23$, and 0.4 meV from the bottom to the top. These spectra were then measured at different temperatures in order to determine evolution of the gaps. The resulting temperature dependences are depicted in Fig.2d by symbols, the color code is kept the same. The lines represent a standard BCS behavior. For the two larger gaps, experimental data follow the theoretical curve in good agreement with no trace of tailing effect, yielding the values of $T_c = 6.85$, and 9.2 K, which are lower than the bulk $T_c = 9.9$ K. Together with the gap values, it leads to the strong superconducting coupling ratio $2\Delta/kT_c = 4.15$, and 4.35 respectively. This fact favors surface inhomogeneities scenario. It suggests that in the sample there are local areas with suppressed superconductivity and that these areas are thicker than the coherence length of the sample, otherwise the proximity effect would lead to persistence of superconductivity in the junction up to the bulk $T_c$. The smallest energy gap closes at $\sim 3$ K, a value which is significantly low, yet higher than what would be expected for the strong coupling ratio larger than 4. The dashed line visualizes BCS curve with $2\Delta/kT_c = 4.15$. Obviously, superconducting energy gap survives up to higher temperatures, probably due to some proximity effect.

In some specific cases also two-gap spectra with two pairs of coherence peaks were observed. They were found at the boundaries between the areas with different dominant gap value as demonstrated in Fig.2e. The tunnelling spectra measured along the white line in Fig.2a exhibit a convolution of two separate spectra with different gap width (1.6 meV and 0.6 meV) as expected for the simultaneous tunnelling to two neighboring phases. The relative contributions of the larger and the smaller gap gradually shift, while moving along the line, starting from the larger single-gap spectrum on one side (black symbols in Fig.2e), through two-gap spectra with progressively increasing weight of the smaller gap, ending up with the smaller single-gap spectrum (pink symbols in Fig.2e) on the other side of the line.

Even in a text-book example of the two-gap superconductivity, in MgB$_2$, two-gap spectra were not revealed at any occasion. Both energy gaps were observed only for tunnelling parallel to the $ab$ plane, while in the $c$ direction, only the small energy gap was present in the spectra. This is due to different character of the Fermi surface sheets related to the two energy gaps - while $\pi$ band with the small gap is three-dimensional, the large gap resides on a $\sigma$ band that is quasi two-dimensional. In the spectra in Fig.2e, a small single gap is observed at the protrusion and a single large one at the valley, at the two extremes of the scanned line. In between, at the slope, we see a smooth transition between the two spectra featuring two gaps in each individual curve. In this case, the directionality similar to MgB$_2$ can be excluded. Indeed, in the positions at the valley bottom and the protrusion top the main tunnelling current goes perpendicular to the plane while in between there could be tunnelling both parallel and perpendicular to the plane. In the case of MgB$_2$ the terminal points at the bottom and the top would give a spectrum with the small energy gap from the three-dimensional $\pi$ band while at the slope, thanks to the contribution of the $ab$-plane tunnelling, two gaps would appear in the spectrum. However single-gap spectra with different energy gap values on both ends of the scanned line make this scenario impossible in the case of Mo$_8$Ga$_{41}$. Thus, the observed two-gap spectra are not corresponding to intrinsic two-gap superconductivity, they rather reflect a convolution of two different single-gap contributions mixed in one junction as coming from neighboring areas.

Taking into account the scenario of formation of several surface phases with different energy gaps in the single crystal of Mo$_8$Ga$_{41}$, we also propose a chemical explanation. As was mentioned above, besides Mo$_8$Ga$_{41}$, there is also Mo$_6$Ga$_{31}$, which is superconducting below $T_c = 8$ K in zero magnetic field [12]. Actually, Mo$_8$Ga$_{41}$ and Mo$_6$Ga$_{31}$ compounds can be combined into the Mo$_n$Ga$_{5n+1}$ family of superconductors. The $n = 4$ member, Mo$_8$Ga$_{27}$, was not synthesized as an individual compound, however, it can be stabilized if gallium is partially replaced by a chalcogen. Indeed, Mo$_4$Ga$_{25-1+}S_y$, Mo$_4$Ga$_{32-1+}Se_y$, and Mo$_4$Ga$_{32-1+}Te_y$ compounds have been synthesized, and they show superconducting properties below $T_c \sim 5.2$ K in zero magnetic field [21]. Mo$_8$Ga$_{5n+1}$ compounds exhibit a clear structural relationship. Their crystal structures are close to each other with the difference lying in the way how MoGa$_{10}$ polyhedra are packed and organized. Therefore, we assume that a single crystal of Mo$_8$Ga$_{41}$ may contain domains, where the packing of MoGa$_{10}$ polyhedra is slightly different resembling those in the Mo$_8$Ga$_{5n+1}$ series for $n = 4, 6, 8, 10$. As a consequence of this, the formation of superconducting domains with different energy gaps may be seen. Remarkably, domains different from the main phase are really minute since our precise single-crystal X-ray diffraction experiments showed no deviations from the Mo$_8$Ga$_{41}$ crystal structure.

In summary, in this work we performed a detailed study of superconductivity in Mo$_8$Ga$_{41}$ with $T_c = 9.9$ K by means of bulk and surface sensitive techniques, i.e. highly sensitive ac calorimetry and scanning tunnelling microscopy/spectroscopy.
applied on the same single crystal. Heat capacity of the system measured in zero magnetic field is characteristic for a strong-coupling single-gap superconductor with the coupling ratio $2\Delta/kT_c \sim 4.4$. Detailed research have shown that Mo$_8$Ga$_{41}$ samples, where the zero field heat capacity measurements evidence the single-phase superconductivity can reveal weak multiphase character in the presence of applied magnetic field. Splitting of the superconducting transition anomaly is evident in high magnetic fields at low temperatures. Presence of the multiphase superconductivity is clearly visible on the surface of the studied samples, where our local STM measurements reveal broad distribution of the superconducting energy gap, which scale with $T_c$ in the strong coupling limit $2\Delta/kT_c \sim 4.25 \pm 0.1$. Thus we conclude that there is only one intrinsic energy gap in the system featuring strong electron-phonon coupling.

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