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ABSTRACT

An observed correlation between the critical temperature of a superconducting transition in high-temperature superconductors and a proximity of their electronic structure to the topological Lifshitz transition needs to be verified on simple model materials. Here we show that such an object could be a Mo–Re alloy with an equal concentration of constituent elements. We present new evidence of the presence of two energy gaps in this material, obtained using point-contact spectroscopy, and argue that the studied Mo–Re alloy can be used for implementing new quantum effects associated with the phase difference of electron wave functions from the different bands.

1. INTRODUCTION

Theoretical approaches describing the properties of crystalline materials often use an idealized one-band model of the electronic structure. When the multiband effects are taken into account, they usually play a minor role, which is limited to improving a correspondence of calculated and experimental data. At the same time, the multiband nature of the most functional materials, promising for practical applications, may not be reduced to a trivial increase in the number of adjustable parameters but is rather more fundamental. This fully applies to superconducting metals, for which a multiband modification of the BCS theory was proposed in 1959[1] but was remained practically un-claimed until the discovery of superconductivity in magnesium diboride at the beginning of the century. In this material, two distinct groups of carriers with fundamentally different properties were discovered for the first time. The two energy gaps in the spectrum of elementary excitations below the critical temperature of the superconducting transition, T_c, differ by almost three times.[2]

Similar finding also applies to superconducting cuprates with relatively high T_c, which can be described by the standard single-band BCS theory or its generalization to the case of strong electron-phonon coupling only as a first approximation. The subsequent discovery of superconductivity in iron-containing compounds[3] has showed that high-temperature superconductors are fundamentally multi-band and there is a certain correlation between T_c and a proximity of the electronic structure of such metals to the topological transition of the Lifshitz type.[4–6] Despite the solid experimental evidence for such a correlation and certain efforts of theorists,[7,8] there is still no microscopic theory able to explain key mechanisms of this relationship and to provide specific recommendations for increasing T_c by controlled modification of the metal band structure. In this case, the main problem is that corresponding consistent theory should take into account a large number of factors, namely, the geometry of the band structure, interaction between electrons and other excitations in the crystal, fluctuation effects, dissipative processes, *etc.* Therefore, preliminary conclusions obtained mainly for the high-temperature superconductors require systematization and testing on new (more simple) systems.

In our opinion, the molybdenum-rhenium alloy with a critical temperature T_c up to 15 K can be such an object. Recently, due to unique mechanical and chemical properties of the compound, in which superconductivity was discovered in 70 s of the last century, interest for the Mo–Re alloys has revived. Nowadays there are several convincing proofs that at certain concentrations of rhenium in the alloy, a topological Lifshitz transition takes place and, as a result, two energy gaps appear in the superconducting state. In the next section, we present a brief literature review of experimental

studies of the Mo–Re alloy directly related to the issue under discussion. Then, the details of our point-contact experiments with the Mo–Re alloy are presented. The next section is devoted to the analysis of the experimental data that indicates the presence of two-gap superconductivity in this material even in the case when there is an equal amount of the two constituent elements. The main results of the work are summarized in the Conclusions.

2. ELECTRONIC STRUCTURE OF THE MO–RE ALLOY

In 1960[9] I. M. Lifshitz has drawn attention to the fact that a change in the Fermi surface topology (electronic topological transition) in a metal caused by deformation of the band structure leads to nonlinear changes in electronic and thermodynamic characteristics of the material. The influence of the topological transition of Lifshitz type on superconducting characteristics was revealed experimentally in 1965 for non-transition metals with small additions of impurities, and subsequent experiments made it possible to establish a correlation between the corresponding behavior of the normal and superconducting properties of metals, see the paper[10] and references therein. Moreover, it turned out that any external influence (not only pressure, but addition of impurities and even temperature) can be an effective means of affecting the topology of the Fermi surface, and, therefore, on the superconducting properties. The most surprising result was that even in alloys with high concentrations of scattering centers (impurities) their effect was not as important as that of relatively small variations in the density of electronic states.[11] This circumstance was first demonstrated just on molybdenum- rhenium alloys (see Ref. 10 for details), where the addition of Re impurity to pure Mo led to a growth in the electron concentration, thereby bringing the Fermi level closer to the critical energy of the electronic spectrum of molybdenum. Note that, along with the topological transition at a fixed rhenium concentration, oscillations of T_c with pressure and oscillations of the temperature dependence of the resistivity $\rho(T)$ have been observed as well.[10]

According to Ref. 10, in Mo–Re alloys, two successive transformations of the electron spectrum take place: the appearance of a new Fermi-surface cavity at a rhenium concentration of $c_0 \sim 10$ at. %, and then partial localization of electrons belonging to the new *d*-group. The latter fact leads to softening of the phonon spectrum in Mo–Re alloys in the region of rhenium concentrations exceeding c_0, and, consequently, to an enhancement of the electron-phonon interaction, as was found by the point-contact spectroscopy approach by Tulina and Zaitsev.[12] It can be assumed that just this factor is the primary source of the T_c enhancement with the subsequent addition of rhenium up to the values of $T_c < 15$ K that are unusually high for traditional superconductors. Also note, that considerations about the localization of new electronic states, arising as a result of the Lifshitz topological transition, have remained speculative until recently, and convincing evidence of the phenomenon proved by resonant photoemission spectroscopy was obtained by the authors of the work[13] only in 2020.

The purpose of the above brief review was to substantiate the importance of detailed studies of the electronic spectrum of a Mo–Re alloy in a superconducting state. If a topological Lifshitz transition does indeed take place upon the addition of rhenium, then the appearance of a second energy gap in the spectrum of quasiparticle states in a Mo–Re superconductor is quite probable. In our recent paper,[14] we demonstrated the presence of two gaps in the $Mo_{0.65}Re_{0.35}$ alloy by tunneling spectroscopy. Similar conclusions established two-gap superconductivity in molybdenum-rhenium alloys by other experimental methods could be found in Ref. 14. The values of the larger $\Delta_l = 2.5$ meV and smaller $\Delta_s = 0.5$ meV energy gaps found by us in Ref. 14 were in good agreement with 2.3 and 0.7 meV as well as with 1.9 and 0.5 meV for a $Mo_{0.6}Re_{0.4}$ alloy. They also agreed well with the data for the temperature dependence of the electronic heat capacity and that for the density of the superconducting component.[15]

In this paper, we present new evidence of the presence of two significantly distinct energy gaps in a Mo–Re alloy with approximately equal component concentrations that has been revealed by the point-contact spectroscopy experiments. Note that this material has been earlier studied using this method only in the normal state.[12]

3. EXPERIMENTAL

Extremely low oxidizability of the molybdenum-rhenium alloy[16] is well known as it does not allow to create tunnel barriers on the surface of Mo–Re samples in a natural way. However, for the point-contact spectroscopy, this restriction is, on the contrary, extremely useful, since it makes it possible to study the spectrum of quasiparticle excitations directly in the near-contact region of such a superconductor. Another advantage of this technique is that using the basic idea of Andreev reflection from the interface between normal (*N*) and superconducting (*S*) metals,[17] we are able to interpret the measured characteristics qualitatively without involving complex model concepts. In an ideal *N/S* contact, an electron incident from the normal side can be reflected back as a hole excitation and vice versa (Andreev reflection). For voltages below the gap, it is the only way to penetrate the superconductor. Therefore, the differential conductivity of the *N/S* contact $G(V) = dI(V)/dV$, the derivative of the current I through the contact with respect to the voltage V, doubles its normal-state value for $V < \Delta/e$ (e is the elementary charge). In the case when a potential barrier arises between the two electrodes, the shape of the $G(V)$ curve changes radically—a maximum appears at $V = \Delta/e$, which becomes more pronounced in the tunneling limit, corresponding to a very small probability of an electron to transmit the *N/S* interface.

In our experiments, the *N*-electrode was usually made of silver, its point contacts with the studied Mo–Re alloy were created both on film and bulk samples (a small part of the measurements was performed using a needle made of Mo–Re alloy and pressed against the silver film). Thin layers of a molybdenum-rhenium alloy with an approximately equal concentration of components, thickness ranging from 90 to 150 nm, and critical temperatures about 9 K were obtained by magnetron sputtering of a $Mo_{0.52}Re_{0.48}$ target with an average deposition rate of 0.5 nm/s in the vacuum of $3 \cdot 10^{-2}$ Pa. The substrates have been made of Sitall or sapphire. The structure and phase composition of the obtained films have been controlled by electron microscopy and electron diffraction, as well as by x-ray diffraction. The concentration of alloy components in the films determined using x-ray photoelectron spectroscopy with an accuracy of 5–6 at. % well corresponded to the target composition. In the substrate temperature T_s range from 300 to 820 K, the films

were polycrystalline with a bcc lattice. The grain size depended on the T_s value and was approximately 10 nm at $T_s \approx 300$ K and 40–60 nm at T_s from 870 to 920 K. Grain size spread was found to be tiny. This uniformity contributed to high resistance of the films to structural transformations and stable electrophysical properties during thermal cycling. Current-voltage characteristics and their voltage derivatives have been measured using a standard four-probe circuit. More experimental details can be found in the paper.[18]

As is well known, the normal-state point contact resistance R_{pc} of a circular constriction in an insulating diaphragm separating two conducting half-spaces is controlled by the ratio of the orifice radius a and the mean free path l.[19] In the diffusive regime, when a is much larger than l, Maxwell found that $R_{pc} = R_M = \rho / (2a)$, where ρ is the resistivity of the conductor on each side of the diaphragm. In the opposite ballistic limit, the conductance G_{pc} is a product of the conductance quantum $2e^2/h = 7.75 \cdot 10^{-5}$ S and the number of quantum channels. This leads to the Sharvin formula $R_{pc} = R_S = (2h/e^2)/(ak_F)^2$ with k_F, the Fermi wavenumber of the conductor. In the intermediate regime, when $a \simeq \ell$, Wexler[19] showed that the crossover from R_M to R_S can be described by the relation

$$R_{pc}(T) = \frac{2h/e^2}{(ak_F)^2} + \Gamma(l/a)\frac{\rho(T)}{2a}, \quad (1)$$

where $\Gamma(l/a)$ is a numerical factor close to unity. Numerical calculations for the Mo–Re compound[20] show that the absolute value of the Fermi wave vector considerably depends on its direction and roughly satisfies the inequality $k_F < 10\ \text{nm}^{-1}$. Measurements of the resistivity $\rho(T)$ of polycrystalline samples of $Mo_{1-x}Re_x$ alloys, for $0 \le x \le 0.4$,[21] give us the following value for Mo–Re samples with an equal concentration of the components: $\rho(0) \approx 10\ \mu\Omega\cdot$cm. Now we can estimate the size of the point contacts, the conductance spectra of which are shown below in Figs. 1 and 2. For the samples with the normal-state resistances 5.4 Ω and 3.1 Ω we get $a \approx 15.4$ and 23.3 nm, respectively, the values of the order of the grain sizes. Both contributions to the R_{pc} resistance (1) are comparable in magnitude, but the second is noticeably superior to the first, i.e., we are dealing rather with the diffuse transfer through the contact.

4. MEASUREMENT RESULTS AND THEIR DISCUSSION

The measured differential conductance spectra $dI(V)/dV$ of contacts based on Mo–Re alloys with approximately equal component contents could be divided into two main groups, the examples of which are shown in Figs. 1 and 2. In both cases, we revealed the presence of two energy gaps, larger Δ_l and smaller Δ_s ones. The first group of spectra (Fig. 1) represent a sum of two similar characteristics of N/S contacts with an almost ideal interface, while the other (Fig. 2) can be interpreted as a contribution of two spectra, wherein the one corresponding to a smaller gap clearly indicates the presence of a small barrier on the N/S interface. In addition, noticeable differences have been observed in the values of the energy gaps Δ_l and Δ_s for two groups of contacts (compare Figs. 1 and 2). This fact, apparently, is the result of significant anisotropy of the two electronic bands determining the $I(V)$ characteristics of the heterostructures under study, similar to magnesium diboride.[22] Note also that the small barriers were usually observed for samples

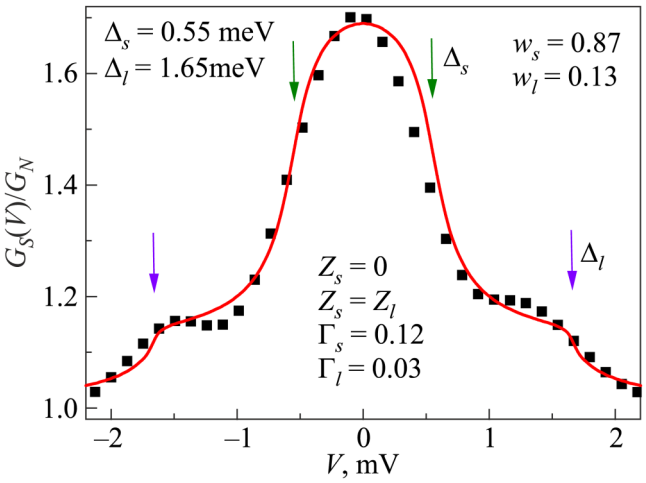

FIG. 1. Differential conductance $G_S(V) = dI_s(V)/dV$ of a representative sample from the first group of contacts formed by a silver tip and a Mo–Re alloy film. The $G_S(V)$ curve is normalized to the contact conductance in the normal state $G_N = 1/R_N = 0.19$ S. The contact parameters Z and Γ for the two electron bands are practically identical, while the energy gaps differ markedly: $\Delta_s = 0.55$ meV and $\Delta_l = 1.65$ meV, the contribution of the band with a smaller gap is dominant, the measurement temperature was 4.2 K.

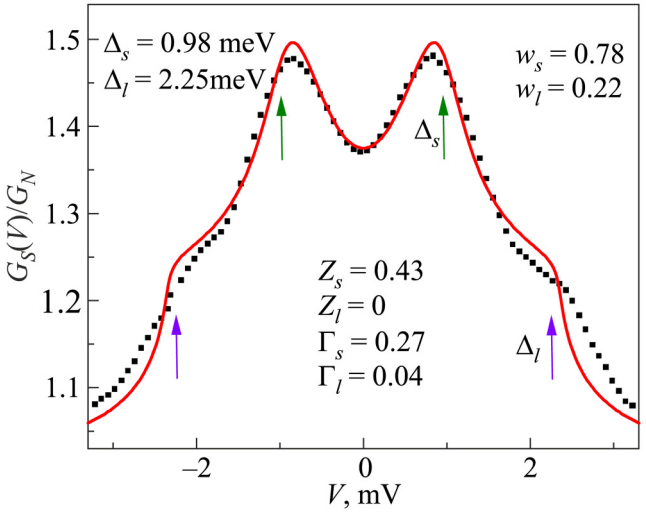

FIG. 2. Differential conductance $G_S(V) = dI_S(V)/dV$ of a representative sample from the second group of contacts formed by a silver tip and a Mo–Re alloy film. The $G_S(V)$ curve is normalized to the contact conductance in the normal state $G_N = 1/R_N = 0.32$ S. The contact parameters Z and Γ for two electron bands differ significantly from each other, as well as the energy gaps $\Delta_s = 0.98$ meV and $\Delta_l = 2.25$ meV, the contribution of the band with a smaller gap is dominant, as in Fig. 1, the measurement temperature was 4.2 K.

with lower normal-state resistances R_{pc}, i.e., with larger orifice sizes. Possibly, this finding is due to the fact that the contact was actually formed with two grains of different orientations or its interface has been substantially inhomogeneous.[23,24] This can be the reason for different barrier strengths in the second group of samples ($Z_s \neq Z_l$ in Fig. 2, see the definition of the parameter Z below).

In our case, due to the small area of contacts, we got an information only from individual micro-sized crystallites with different crystallographic directions, while, say, measurements of the electronic heat capacity for a molybdenum- rhenium alloy[15] give characteristics averaged over all directions. Local changes in superconducting properties in the near-surface region may be another source of the differences between surface-sensitive techniques and those dealing with the bulk.[25,26]

The most popular way for interpreting the conductance spectra $G_S(V) = dI_S(V)/dV$ is the Blonder–Tinkham–Klapwijk model,[27] which assumes the ballistic and onedimensional character of electron transport and describes the scattering at the N/S boundary using the parameter $Z = U_0 / (\hbar v_F)$, where $U_0\delta(x)$ is the effective potential localized at the interface, and v_F is the Fermi velocity.[28] Ultimately, the parameter Z determines the probability of electron transmission through the barrier $D_N = 1/(1 + Z^2)$ in the normal state as well as the reflection probability $R_N = 1 - D_N = Z^2/(1 + Z^2)$. In the case of a single-band superconductor, the general formula for calculating the ratio of differential conductance in superconducting and normal states reads as:[22]

$$\frac{G_S(V)}{G_N} = 1 + \frac{1 + D_N|\gamma(E)|^2 - R_N|\gamma^2(E)|^2 - |1 - R_N\gamma^2(E)|^2}{|1 - R_N\gamma^2(E)|^2}, \quad (2)$$

where $\gamma(E) = \Delta/(E + \sqrt{E^2 - \Delta^2})$, $E = eV$ the normal conductivity G_N is proportional to the D_N magnitude. Additionally, we introduce a constant imaginary part in the electronic energy $E \to E + i\Gamma$, where Γ is the so-called Dynes parameter, determined by the conditions of sample preparation and the temperature of the experiment. Such a replacement was justified, in particular, in the paper,[29] where the inelastic-scattering processes in a superconductor were taken into account. As a result, we have three adjustable parameters in a single-band superconductor, the energy gap Δ, the interface scattering efficiency Z, and the Dines parameter Γ. In the case of a two-band superconductor, this number increases to seven: Δ_l, Δ_s Z_l, Z_s, Γ_l, Γ_s and, finally, the weighting factor $w_l < 1$ ($w_s = 1 - w_l$), which specifies the relative contribution of the two bands to the measured curve $G(V) = w_lG_l(V) + w_sG_s(V)$. Corresponding values of these parameters at which the total curve $G_S(V)$ in the superconducting state best describes the experimental data are shown in Figs. 1 and 2.

The results obtained convincingly indicate the presence of two energy gaps in the spectrum of quasiparticle states in the studied superconducting molybdenum-rhenium alloy. This is the first observation of a two-band superconductivity in Mo–Re alloys with a rhenium concentration exceeding 40 at. %, a range where electronic heat capacity measurements[30] indicated a conventional single-band superconductivity.

5. CONCLUSIONS

Tunneling[14] and point-contact (this work) experiments demonstrate the presence of two energy gaps in superconducting Mo–Re alloys with approximately equal component concentrations. The rather large ratio $2\Delta_l/k_BT_c$ for a larger gap indicates strong electron-phonon coupling, at least, on the surface of this compound.[25] In addition to the evident goal of increasing T_c, the existence of several superfluid Cooper-pair condensates with different order parameters and a weak Josephson coupling between them makes it possible to use this material for studying new quantum-coherent states which may manifest itself in a number of specific quantum phenomena associated with the phase difference of the wave functions of different electronic condensates.[31,32] These may include collective modes of oscillations of the order-parameter phase difference and the density of Cooper pairs from two bands, formation of composite Abrikosov vortices in a mixed state caused by superfluid currents from different bands, *etc*. We believe that the Mo–Re alloy with approximately equal concentration of the components can serve as a perfect test case for studying the above effects, investigating time-reversal symmetry breaking in unconventional superconductors[33] and specific superconducting boundary states in multiband systems,[26] developing novel superconducting devices[34] and practical recipes for increasing T_c of superconductors by purposefully changing their band structure.

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