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New superconducting phases in $Mo_2Re_3B_x$–$Mo_3Re_2B_x$ eutectic*

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We report on the discovery and on some basic properties of the eutectic alloy composed of two new superconducting phases; $Mo_2Re_3B_x$ with T_c = 8.7 K and of $Mo_3Re_2B_x$ with T_c = 6.6 K (where $x \approx 1$). The two phases in the eutectic form complex globular structure and areas of locally ordered lamellar patterns. The lamellae are separated by thin interface of excess boron and behave like a regular network of Josephson junctions. Distinct two-step superconducting transition indicates that this eutectic belongs to inhomogeneous systems with no evidence for the proximity effect. The parameters of the dominating $Mo_3Re_2B_x$ phase are as follows: the lower and the upper critical fields are equal to μ_0H_{c1} = 13 mT and to μ_0H_{c2} = 6.5 T, respectively. This corresponds to the penetration depth λ = 2040 Å, to the coherence length ξ = 70 Å and to Ginzburg –Landau parameter κ = 29. Linear temperature dependence of $H_{c2}(T)$ may be due to unconventional mechanism of superconductivity in dominating $Mo_3Re_2B_x$ phase.

Key words: *intermetallic compounds; eutectics; superconductor; critical field*

1. Introduction

Boride compounds are promising superconductors because they exhibit high frequency vibration of lighter elements and strong electron-phonon interaction which may lead to enhanced critical temperatures. The best candidates for superconductors should be AB_2-type diborides, but none of the systems with light alkali metal A = Li, Be or Al exhibit superconductivity. Except MgB_2 with a record critical temperature equal to T_c = 39 K [1], there was reported only low temperature superconductivity in

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heavy metal diborides like $BeB_{2.75}$ with $T_c = 0.72$ K [2], NbB_2 ($T_c = 3.87$ K) [3], TaB_2 ($T_c = 9.5$ K) [4] and in ZrB_2 below 5.5 K [5]. Superconducting systems with rhenium are also known, for example ReB ($T_c = 2.8$ K) [6], Re_3B ($T_c = 4.7$ K), ReB_2 ($T_c = 4.5$–6.3 K) [7] and Re_7B_3 with $T_c = 3.3$ K [8].

Superconductivity appears also in ternary MReX type compounds where M = Mo, W and X = B, C [9, 10]. Examples are $W_7Re_{13}B$ and $W_7Re_{13}C$. Some superconducting materials can be obtained in a form of eutectics in which superconducting phase is embedded in a matrix phase. The matrix phase can be normal metal, another superconductor, semiconductor or dielectric and it strongly influences basic superconducting properties of the eutectic [11]. The behaviour of eutectic also depends on geometry and structure of the superconducting and normal phases. In general, eutectics exhibit two extreme behaviours: properties of eutectic can be more or less a simple sum of properties of the two phases [12] or it can behave as a completely homogeneous system due to the proximity effect [13]. Fine superconducting structures (for example lamellae) in an eutectic separated by normal or insulating matrix sometimes can form network of the Josephson junctions [14]. In the present paper, we report on superconductivity in $Mo_2Re_3B_x$–$Mo_3Re_2B_x$ eutectic system composed of new, superconducting phases.

2. Experimental

$Mo_2Re_3B_x$–$Mo_3Re_2B_x$ eutectic has been synthesized by the method of induction melting of the constituent elements under argon atmosphere in a water-cooled boat. Fine powders of Mo, Re and B with the total mass about 1 g were used for the alloying. To ensure homogeneity, the ingot was inverted and remelted several times. In spite of this procedure, we found nonstoichiometric phases and excess of rhenium near the surface of the ingot. Thus, the investigated sample was cut from the interior of the ingot.

The microstructure and composition of the sample was investigated using Zeiss Ultra 55 scanning electron microscope (SEM) equipped with energy dispersion spectroscopy (EDS) probe. Magnetometric measurements were performed by means of Quantum Design MPMS SQUID magnetometer and also by Oxford Instruments Ltd. MagLab 2000 System. The magnetic measurements were corrected for demagnetizing effect. The demagnetizing coefficient N of the investigated sample was assumed to be 0.22. Quantum Design PPMS 7T bridge and a standard four point contact method were used for the electric transport measurements. The current strength was equal to 1 mA.

3. Results and discussion

An eutectic system arises during solidification of an initial melt, when two phases in the melt do not form a solution for any relative concentration. An example of the polished surface of our eutectic sample is presented in Fig. 1. There are visible large globules or grains of the grey phase with dimensions of a few tenth of μm separated by regions composed of lamellae of the two phases – grey and black one. The details of lamellar structure, which is typical of some eutectic systems, are presented in the inset to Fig. 1.

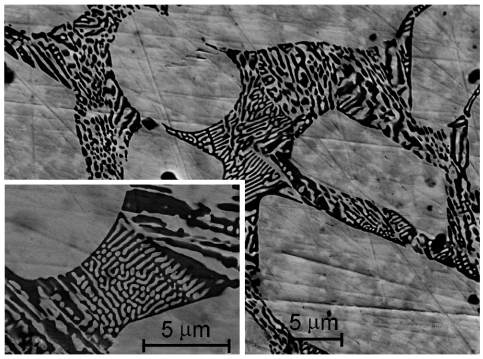

Fig. 1. The SEM micrography of $Mo_2Re_3B_x$–$Mo_3Re_2B_x$ sample. Inset: the example of regular lamellar structure between globules of $Mo_3Re_2B_x$ phase

The eutectic exhibits some similarity to granular superconductors composed of grains separated by normal matrix because at interfaces between the two phases there exists a normal layer of metallic boron. This conclusion is confirmed by the eutectic resistivity dependence in a wide temperature range shown in Fig. 2. The resistivity of this eutectic is rather high as for metals and it decreases gradually with temperature. The residual resistivity ratio (RRR), which defines resistivity changes versus temperature; RRR = R(10 K)/R(300K) is also high and equal to 0.7. The semiconducting layer of boron deposited at interfaces increases significantly resistivity of the system and makes it almost independent of temperature. An identical behaviour was found in similar ternary borides $W_7Re_{13}B$ and $Mo_7Re_{13}B$ and explained in the same way [9, 10].

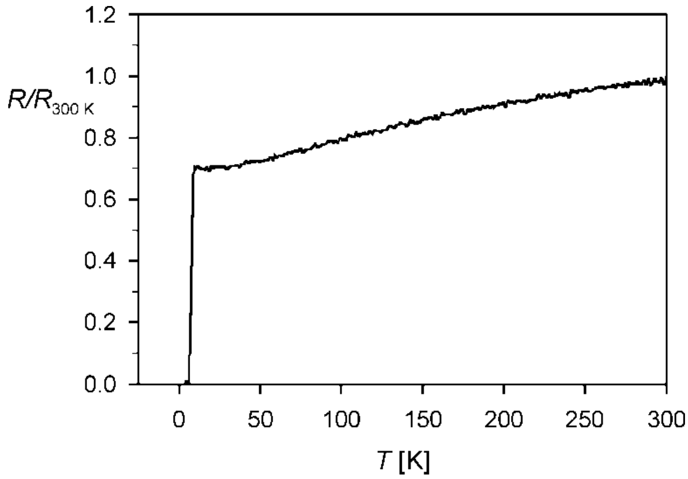

Fig. 2. The temperature dependence of normalized resistivity $R(T)/R(T = 300\text{ K})$ of $Mo_2Re_3B_x$–$Mo_3Re_2B_x$ eutectic

In the lamellar regions, a regular Josephson junction network exists, which is confirmed by very strong absorption of microwave energy observed in this eutectic [15]. Large grains of grey phase dominate in the alloy, because the initial melt was probably shifted out of the optimal eutectic composition. The chemical compositions of the two phases were determined by means of EDS, based on the energy spectrum and the relative intensities of X-ray radiation. The grey phase was identified as $Mo_3Re_2B_x$ compound and the black phase as $Mo_2Re_3B_x$. The accurate determination of boron content was difficult because of low energy of the boron line and small dimensions of the black lamellae which were almost at the limit of the spatial resolution of the electron beam. The detailed discussion devoted to identification of phases in this eutectic was presented in ref. [15]. There is no trace of $Mo_7Re_{13}B$ phase reported earlier by Kawashima [10] in the EDS spectra, probably due to different thermal conditions during the alloying process.

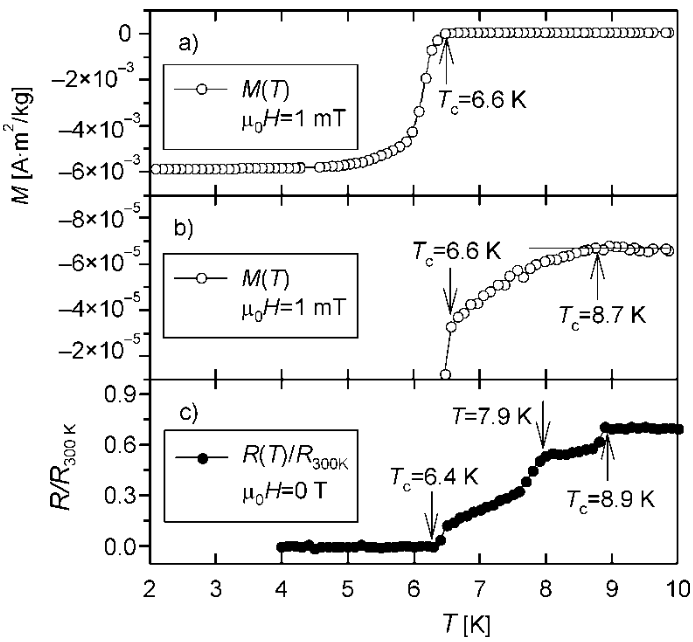

Fig. 3. Superconducting transition in the eutectic system; the magnetisation $M(T)$ vs. temperature (a), the details of superconducting transition (b) and the resistive superconducting transition (c)

The details of superconducting transition in magnetic and electric properties are shown in Fig. 3. The diamagnetic moment appears below 6.6 K (Fig. 3a), however a subtle drop of the magnetic signal occurs also at higher temperature equal to 8.7 K (Fig. 3b). The main superconducting transition is quite sharp with the transition width at 50% of diamagnetic moment equal to 0.4 K. The double-step nature of superconducting transition is more clearly seen in the resistivity dependence on temperature (Fig. 3c). The first step in resistivity occurs at 8.9 K which corresponds well to the subtle transition at 8.7 K in magnetic properties. The sample looses resistivity at 6.4 K, slightly below the temperature of the main superconducting transition. There is also another feature in the electrical resistivity at 7.9 K.

The complex nature of superconducting transition is caused by the presence of two superconducting phases and by the structure of this eutectic. The transition at higher temperature is related to the black lamellae of $Mo_2Re_3B_x$ phase characterised by a small volume but large extent. In the magnetic properties, this phase is almost unnoticeable because of its negligible volume but it shunts electrically large part of the sample due to its elongated shape. The superconducting transition in the dominating grey $Mo_3Re_2B_x$ globules leads to a sudden appearance of a diamagnetic signal at 6.6 K and also shunts totally the sample below 6.4 K. The drop in electrical resistivity observed at 7.9 K is an effect of electrical percolation in the system of $Mo_2Re_3B_x$ lamellae.

Two distinct different superconducting transitions indicate that the whole eutectic behaves like an inhomogeneous system with properties which are more or less a simple sum of the properties of the two phases. Also the proximity effect is rather absent in this case. This allows one to investigate and to separate some physical properties belonging to each phase present in the eutectic [12]. However, the amount of $Mo_2Re_3B_x$ phase is too low to determine any parameter except the critical temperature. Therefore, in this report we determine basic parameters like critical fields, coherence and penetration depth for the dominating $Mo_3Re_2B_x$ phase only. The dependence of the upper critical field on temperature, $H_{c2}(T)$, of $Mo_3Re_2B_x$, equivalent to the $T_c(H)$ dependence is shown in Fig. 4.

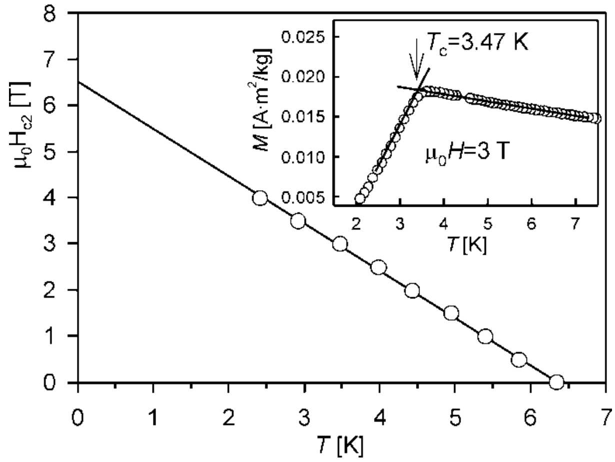

Fig. 4. Upper critical field $H_{c2}(T)$ for $Mo_2Re_3B_x$–$Mo_3Re_2B_x$ eutectic. The inset presents the way of determination of the critical temperature $T_c(H)$ for a selected magnetic field (3 T in this case)

The critical temperatures corresponding to selected magnetic fields $T_c(H)$ are determined from the intersection of two straight lines fitting the relevant linear regimes of $M(T)$ curves above and below the superconducting transition, respectively (see inset to Fig. 4). Surprisingly, the best fit to the field $H_{c2}(T)$ experimental data is obtained using the linear relation; $H_{c2}(T) = H_{c2}(0)(1 - t)$ where t is the reduced temperature $t = T/T_c$. The usual parabolic dependence [16, 17]; $H_{c2}(T) = H_{c2}(0)(1 - t^2)$ is invalid in this case. This may indicate an unconventional mechanism of superconductivity in $Mo_3Re_2B_x$. A similar linear dependence of $H_{c2}(T)$ is observed in MgB_2 [18, 19], $BeB_{2.75}$ [2] and in ZrB_{12} [5]. From the best linear fit one obtains the value of the upper critical field $\mu_0H_{c2}(0)$ = 6.5 T and the slope dH_{c2}/dT equal to –1.02 T/K. The upper critical field estimated from the Werthamer–Helfand–Hohenberg formula [20]; $H_{c2}(0) \approx -0.69T_c(dH_{c2}/dT)$ for this value of slope and for T_c = 6.4 K is much lower than the experimental result and equal to $\mu_0H_{c2}(0)$ = 4.5 T. However, both values are well below the paramagnetic limit $\mu_0H_p = 1.84T_c$ which is equal to 11.8 T. This suggests that other mechanisms than pair breaking due to Zeeman coupling limit the value of the upper critical field in Mo_3Re_2B. Another basic parameter, namely the coherence length ξ can be calculated from the relationship: $\mu_0H_{c2} = \Phi_0/2\pi\xi^2$ where $\Phi_0 = 2\times10^{-15}$ Wb is flux quantum. For μ_0H_{c2} = 6.5 T it is equal to 70 Å.

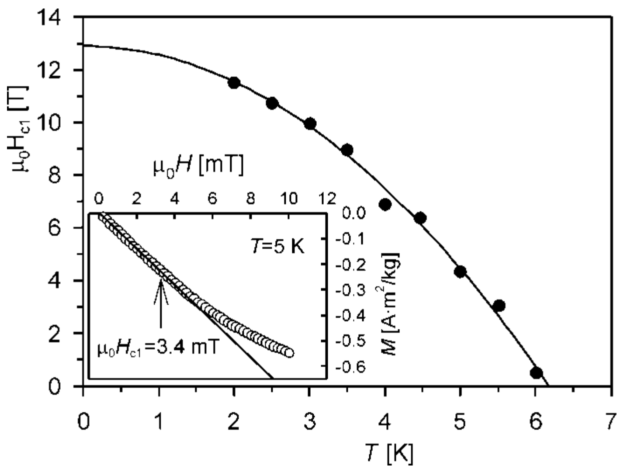

Fig. 5. The lower critical field $H_{c1}(T)$ corrected for the demagnetising effect. The inset shows the magnetisation versus applied magnetic field $M(H)$ for 5 K and the criterion for determination of $H_{c1}(T)$. The data in the inset are as measured (not corrected)

The values of lower critical field of Mo_3Re_2B for selected temperatures may be determined using as a criterion the deviation from linearity of the initial part of magnetization $M(H)$, which is presented in the inset to Fig. 5. The dependence of lower critical field on temperature $H_{c1}(T)$ corrected for the demagnetizing effect is shown in Fig. 5. It is evident that the lower critical field exhibits usual negative curvature and can be well fitted with the parabolic function $H_{c1}(T) = H_{c1}(0)(1 - t^2)$. The parameter of the best fit $\mu_0H_{c1}(0)$ is equal to 13 mT. Based on the equation $\mu_0H_{c1}(0) = (\Phi_0/4\pi\lambda^2)\ln(\lambda/\xi)$, the value of $H_{c1}(0)$ corresponds to the penetration depth equal to λ = 2040 Å. Knowing the coherence length ξ and the penetration depth λ, we can calculate the Ginzburg–Landau parameter $\kappa = \lambda/\xi$. It amounts to 29, being rather high as for intermetallic superconductors.

4. Conclusions

We have synthesized and investigated basic properties of an eutectic alloy composed of two new superconducting compounds, namely of $Mo_2Re_3B_x$ and $Mo_3Re_2B_x$ phases. The SEM examination of the surface of the eutectic revealed complex globular structure and areas with locally ordered lamellae. The two phases are separated by thin layer of metallic boron, which leads to enhanced resistivity of the eutectic. Ordered lamellae of $Mo_2Re_3B_x$ and $Mo_3Re_2B_x$ phases form a regular network of the Josephson junctions.

This eutectic belongs to inhomogeneous systems with no proximity effect, which allows one to investigate the properties of each phase separately. Accordingly, the superconducting transitions at 6.6 K and 8.7 K can be associated with $Mo_3Re_2B_x$ and $Mo_2Re_3B_x$, respectively. The critical fields of the dominating $Mo_3Re_2B_x$ phase are μ_0H_{c1} = 13 mT and μ_0H_{c2} = 6.5 T. This corresponds to the penetration depth λ = 2040Å, to the coherence length ξ = 70 Å and to the Ginzburg–Landau parameter κ = 29. The amount of $Mo_2Re_3B_x$ phase is too low to determine any parameter except the critical temperature. Linear temperature dependence of $H_{c2}(T)$ observed in $Mo_3Re_2B_x$ phase may be due to an unconventional mechanism of superconductivity.

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