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Superconducting properties of $W_7Re_{13}B$ compound

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Abstract

We present both experimental and theoretical investigations of the magnetic properties and electronic structure of the recently discovered superconductor $W_7Re_{13}B$. We determine the lower and the upper critical fields $H_{c1}(0) = 8.77$ mT and $H_{c2}(0) = 11.8$ T, which correspond to a penetration depth $\lambda = 2675$ Å and to a coherence length $\xi = 52$ Å. The Ginzburg–Landau parameter, κ is equal to 51. The effect of pressure on $W_7Re_{13}B$ is negligible. This can be attributed to small changes in the density of states under pressure, or alternatively, to a low compressibility of this hard compound.

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1. Introduction

One of the reasons for the great deal of work on unconventional and also low-temperature superconductors observed in recent years is due to the fact that they may be helpful in explaining the problem of high-temperature superconductivity. The systems studied include the binary Re–B compounds, such as the superconducting intermetallics Re_3B, Re_7B_3 [1] and the nonsuperconducting ReB_3, ReB_2. The Re_2B compound with unknown structure exhibits superconductivity below the critical temperature $T_c = 2.8$ K [2]. Superconductivity in the ternary compounds M–Re–B was discovered by Kawashima et al. [3]. Examples are $W_7Re_{13}B$ and $W_7Re_{13}C$ with critical temperatures $T_c = 7.1$ K and 7.3 K, respectively. However, these materials were first synthesized and their structural properties established almost 30 years ago by Kuz'ma [4]. The crystal structure of $W_7Re_{13}B$ is cubic, β-Mn-type, space group $P4_132$. Tungsten atoms occupy the 8(c) sites and rhenium atoms the 12(d) sites, while boron atoms occupy about one quarter of the octahedral voids and thus stabilize the structure. Recently, the group of Kawashima also reported superconductivity in similar systems, namely in the compounds $Mo_7Re_{13}B$ with $T_c = 8.3$ K and $Mo_7Re_{13}C$ with $T_c = 8.1$ K [5].

One of the main obstacles to investigating the physical properties of these compounds are impurity phases [5,6]. In this article we report on the superconducting properties and high-pressure effects in a $W_7Re_{13}B$ sample obtained using different method to Kawashima et al. [3], which allowed us to avoid the formation of minority phases [7]. We also present theoretical calculations on the influence of pressure on the electronic structure of the compound.

2. Experimental

The $W_7Re_{13}B$ superconducting compound was prepared by the technique of induction melting of the constituent elements in a water-cooled boat, under an argon atmosphere. For the melting, stoichiometric amounts of tungsten, rhenium and boron were used. The ingot was inverted several times to ensure homogeneity. The polycrystalline samples were examined by powder X-ray diffraction using Co Kα radiation. The X-ray spectra did not show any trace of impurity phases. The lattice constant, determined to be equal to 6.820 Å, was in good agreement with the data reported by Kawashima et al. [3].

The X-ray photoemission spectra were recorded using a PHI 5700/660 Physical Electronics Spectrometer and the radiation characterized by the photon

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energy equal to 1487.6 eV (Al Kα source). The measurements were performed immediately after breaking the sample in a vacuum of 10^{-10} Torr. The spectra were analysed by a hemispherical mirror analyzer with a resolution of about 0.3 eV.

The magnetometric measurements under high pressure were performed using a Quantum Design MPMS SQUID magnetometer fitted with an easyLab Mcell 10 high pressure cell. The cell enabled one to apply pressures of up to 1 GPa over a wide temperature range. Due to the solidification point of the pressure medium, which takes place at around 200 K, there was a quasi hydrostatic pressure at low temperatures inside the chamber rather than hydrostatic one. The pressure inside the cell was practically invariant with temperature. Before the measurements, the $W_7Re_{13}B$ sample was ground into a fine powder and placed in a PTFE container together with a pure tin wire manometer (approx. 5mm long and 0.25 mm in diameter). The container was next filled with Daphne oil, sealed and fitted into the high pressure cell. The cell was mounted on a standard SQUID magnetometer sample rod. The magnetic background of the cell was subtracted from the total magnetic signal. The actual pressure in the cell was determined by measuring the shift in the superconducting transition of tin with pressure determined on the basis of magnetic moment measurements versus temperature $M(T)$ at an applied magnetic field of 1 mT. The pressure was evaluated using the polynomial function $P = a[T_c(0) - T_c(P)]^2 + b[T_c(0) - T_c(P)]$, where P is in GPa T in K and the coefficients are equal to: $a = 0.5041489$; $b = 1.781287$ [8].

The other magnetometric measurements such as magnetization versus magnetic field $M(H)$ and temperature $M(T)$ were performed using an Oxford Instruments Ltd. MagLab 2000 ac susceptometer/dc magnetometer. For these measurements a bulk $W_7Re_{13}B$ spherical sample was used.

3. Theory

The electronic structure was calculated for the ordered compound W_8Re_{14} characterised by the space group $P4_132$, No. 213 and lattice constant $a = 6.819$ Å. The unit cell consisted of 20 atoms located at the positions: W (0.061, 0.061, 0.061) and Re (1/8, 0.206, 0.456). In order to simulate the effects of pressure on the density of states (DOS), it was assumed that the positions of atoms and the lattice constant, a, vary within a few percent. The full-potential local-orbital minimum-basis code (FPLO) was used and the band structure was calculated in the scalar-relativistic mode [9]. The calculations were performed using the full potential local orbital minimum basis and the number of k points in the irreductible part of the Brillouin zone was 200. The parametrisation of the exchange-correlation potential in the framework of the local spin density approximation was used in the form proposed by Perdew-Wang [10].

4. Results and discussion

The temperature dependence of the magnetization $M(T)$ of the $W_7Re_{13}B$ superconducting compound at ambient pressure and at applied magnetic field equal to 1 mT is shown in the inset in Fig. 1. The superconducting critical temperature is equal to $T_c = 7.22 \pm 0.02$ K. The width of the transition determined at 50% of diamagnetic signal is equal to ΔT_c (50%) = 0.2 K. Here, critical temperatures at a given applied magnetic field $T_c(H)$ were determined from the intersection of the two straight lines that fit the relevant linear regimes of $M(T)$ curve above and below the superconducting transition, which manifests itself as a sudden decrease of the magnetisation. This allowed us to determine the phase diagram of the $W_7Re_{13}B$ compound because the $T_c(H)$ dependence is equivalent to the temperature dependence of the upper critical field $H_{c2}(T)$ (see Fig. 1). A best fit of the

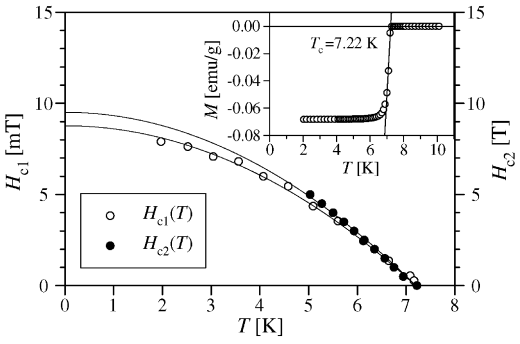

Fig. 1. The temperature dependence of the lower $H_{c1}(T)$ (open points) and upper critical field $H_{c2}(T)$ (filled points). The lines represent the two-fluid model fits to the experimental data. Inset: the superconducting transition of the $W_7Re_{13}B$ compound under ambient pressure and the method for determining the critical temperature.

experimental data is obtained using the Casimir–Gorter two-fluid model [11]; $H_{c2}(T) = H_{c2}(0)(1 - t^2)$ where t is the reduced temperature $t = T/T_c$. The parameters of the best fit are as follows: $T_c = 7.2$ K and $H_{c2}(0) = 9.51$ T. As can be expected, the data exhibits a linear dependence in the vicinity of the critical temperature with the slope $dH_{c2}/dT = -2.38$ T (K). Using the WHH formula [12]; $H_{c2}(0) \cong -0.69T_c(dH_{c2}/dT)$ with the value of dH_{c2}/dT given above and $T_c = 7.22$ K, one estimates a value of $H_{c2}(0)$ equal to 11.8 T. This is slightly above the value obtained from the fit but is still in good agreement with the value $H_{c2}(0) = 11.3$ T reported by Kawashima et al. [3]. From the relationship; $\mu_0 H_{c2} = \Phi_0/2\pi\xi^2$ where $\Phi_0 = 2 \times 10^{-15}$ Wb is flux quantum we find the coherence length $\xi = 52$ Å.

Fig. 1 also shows the temperature dependence of the lower critical field $H_{c1}(T)$. The values of the lower critical field at a given temperatures were found using as a criterion the deviation of initial part of magnetisation $M(H)$ from linearity. In the case of "classical" superconductors characterized by weak pinning and negligible influence of defects, this criterion allows an exact determination of the temperature dependence of the lower critical field $H_{c1}(T)$. However, it is invalid for high-temperature superconductors, in which surface barriers [13,14] and/or surface pinning [15,16], which hinder the penetration of the vortices into the sample, dominate. This leads to the unusual upturn or positive curvature of the lower critical field, especially in a low temperature limit [17].

The H_{c1} measurements were corrected for the demagnetising effect where the shape of the sample was approximated by an ellipsoid to calculate the demagnetising factor. The data representing the lower critical field in Fig. 1 are once again fitted using the two-fluid model used previously with the parameters; $T_c = 7.2$ K and $H_{c1}(0) = 8.77$ mT. Due to the correction for demagnetizing effect, present value of $H_{c1}(0)$ is higher than that evaluated earlier [7]. On the basis of the relation $\mu_0 H_{c1}(0) = (\Phi_0/4\pi\lambda^2)\ln(\lambda/\xi)$ the value of the lower critical field corresponds to a penetration depth equal to $\lambda = 2675$ Å.

The critical temperature dependence with pressure $T_c(P)$ is presented in Fig. 2. Here, the critical temperatures under various pressures were determined using the same criterion as for the upper critical field measurements, i.e. the intersection of the two

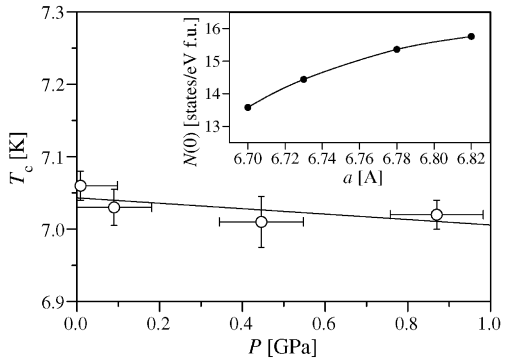

Fig. 2. The dependence of the critical temperature $T_c(P)$ on pressure. The solid line is the best linear fit to the experimental data. Inset: the calculated density of states with respect to the lattice constant a. The solid line is a guide to the eye.

lines fitting the two relevant regions of $M(T)$ curve. Due to the temperature gradient in the thick walls of the high-pressure cell, the $M(T)$ curves are shifted to lower temperatures by 0.14 K with respect to other measurements. The critical temperatures determined from these curves are also lower. In general, in the applied pressure range, the influence of the pressure on the superconducting transition and on the critical temperature is very small.

The theoretical calculations of the dependence of the density of states on the lattice constant a are shown in the inset to Fig. 2. Assuming that hydrostatic pressure causes a contraction of the lattice constant, a decrease of the DOS as the a parameter decreases is equivalent to the influence of pressure. Consequently, due to the BCS relation [18]: $kT_c \sim \hbar\omega \exp[-1/N(0)V]$ (ω is a phonon frequency, $N(0)$ the density of states near the Fermi level and V is the electron interaction), there should be a decrease in the critical temperature if the DOS also decreases under pressure and if V does not change. The relatively small changes in the DOS at the Fermi level (actually less than 14% for a lattice contraction equal to 2%) correspond well with the almost negligible decrease in the critical temperature $T_c(P)$. A second, more trivial explanation of the effect is in terms of low compressibility of this hard material. Thus one needs to use higher pressures to induce observable changes of the critical temperature.

5. Conclusions

The influence of hydrostatic pressure on the superconducting transition of $W_7Re_{13}B$ is negligible due to the small dependence of the DOS on pressure or alternatively due to the low compressibility of this hard compound. The lower $H_{c1}(0)$ and the upper $H_{c2}(0)$ critical fields are equal to 8.77 mT and to 11.8 T, respectively. The penetration depth and the coherence length estimated from the critical field values are equal to: $\lambda = 2675$ Å, $\xi = 52$ Å. The Ginzburg–Landau parameter κ is equal to 51.

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