Giant enhancement of superconductivity in arrays of ultrathin gallium and zinc sub-nanowires embedded in zeolite

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ABSTRACT

We have fabricated superconducting samples comprising gallium (Ga) or zinc (Zn) infiltrated into the one-dimensional (1D) linear channels of AlPO-5 (AFI) zeolite, which have an internal pore diameter of 7 Å and are separated by an insulating wall of ~7–9 Å. The Angstrom-scale Ga and Zn sub-nanowires, arranged in Josephson-coupled triangular arrays with an ab-plane lattice constant of 14.4 Å, display bulk superconductivity with Tc values of 7.2 K and 3.7 K, respectively, which are significantly enhanced by a factor of 7 and 4 compared with their bulk values. While the zeolite template of our composite superconductor dictates the nanostructure of Ga and Zn to be 1D in the electronic sense with a highly advantageous effect for the superconducting pairing, the arrangement in a densely packed array structure avoids the shortcomings of other typical 1D superconductors, in which the coherence is usually completely suppressed by strong phase fluctuations.

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Nanotechnology can tailor the structure of materials in such a way that their characteristics change dramatically. Nanstructuring superconductors can cause unusual effects not known from bulk materials. Examples are the oscillating superconducting transition temperature as a function of the film thickness in Pb films [1] or size-dependent breakdowns of superconductivity, e.g. in Al nanowires [2]. In quasi-zero dimensional fine nanoparticles or nano-granular materials of Ga [3,6,7], In [4,5], and TI [4], enhancements of the superconducting transition temperature were reported. Enhancements in the critical field and temperature were also observed in quasi-one-dimensional (1D) Pb [8–11] and Sn [12,13] nanostructures.

Quasi-1D superconductors are formed by superconducting materials confined in a 1D geometry with a lateral dimensionality smaller than the superconducting coherence length. These materials can be realized either in the form of free-standing individual nanowires or as arrays of parallel nanowires. The latter is found in form of atomic chains in some intrinsic quasi-1D superconductors such as Tl2Mo6Se6 [14] or Sc2CO4 [15]. In addition, arrays of parallel superconducting nanowires have been infiltrated into the pores of mesoporous materials such as SBA-15 silica [8]. Of particular interest are regular, closely spaced arrays of superconducting nanowires, as they can take advantage of quantum confinement and finite size effects within the nanostructure, while some bulk macroscopic superconducting properties such as zero resistance and a measurable Meissner screening effect within the array are maintained by the Josephson coupling between the elements [8,12,16]. While one-dimensionality can have a positive effect on the superconducting parameters, the serious disadvantage is that if the diameter of the nanowire is smaller than the superconducting coherence length, the Mermin-Wagner-Hohenberg theorem [17,18] predicts the suppression of any long-range-ordered physical state by thermal fluctuations. This is because phase-slips in 1D superconducting systems can generate phase changes of 2π across a core region of reduced superconducting condensate, resulting in finite resistance at finite temperatures [19–22]. However, if the Josephson coupling between the 1D superconducting elements is strong enough, a three-dimensional long-range-ordered state can result, as predicted from theory [23–26] and verified by experiments [14,16]. The critical parameter for achieving this long-range-ordered bulk phase-coherent superconducting state in the array is the coherence length, and it has been shown, for example, that...
the crossover in 5-nm NbN nanowire arrays in SBA-15 silica is missing due to its particularly short coherence length, while it exists in Pb nanowires in SBA-15 with identical geometric arrangement [27]. To take advantage of the enhancing effect, it is therefore crucial to select superconducting materials with long coherence lengths, as they occur in elemental superconductors. Only then can a nanostructured superconductor in the technical sense with zero resistance be achieved. While zero-resistance phase-coherent states have actually been reported in nanowire arrays, they are usually only found at very low temperatures far below $T_c$ and in small applied magnetic fields.

In this article, we push the limit of Ga and Zn nanowires to the sub-nanometer range and explore a completely new regime in which Cooper pairs are confined in only a few 100 pm thick wires. The “sub-nanowires” almost approach the limit of a monatomic chain and are very close to each other: embedded in the linear pores of zeolite single crystals, they form a regular array of almost crystalline quality. Bulk Ga and Zn are well-known elemental BCS (Bardeen-Cooper-Schrieffer) superconductors. Nanostructured Ga and Zn superconductors have already been investigated, but only in sizes ranging from a few nanometers to several tens of nanometers. Using zeolite as a template, we have produced Ga and Zn nanowire arrays on the Angstrom-scale. The advantage of using the zeolite template for the Ga and Zn nanostructures is that the zeolite pores are periodically ordered with a precision that can only be the result of a molecular structure. The specific zeolite we used was the AlPO$_4$-5 (AFI) with linear channels along the c-axis, with an inner diameter of 0.74 nm and arranged in a triangular lattice with a center-to-center distance of 1.37 nm in the ab plane. These micro AFI crystallites were synthesized by the hydrothermal method [21]. They are perfect hexagonal platelets with a thickness of ~2 nm, which are periodically ordered with a precision that can only be the result of the molecular structure. The specific zeolite we used was the AlPO$_4$-5 (AFI) with linear channels along the c-axis, with an inner diameter of 0.74 nm and arranged in a triangular lattice with a center-to-center distance of 1.37 nm in the ab plane. These micro AFI crystallites were synthesized by the hydrothermal method [21].

**Zeolite template characterization**

The AFI framework consists of alternating tetrahedral (AlO$_4$)$^-$ and (PO$_4$)$^{2-}$ groups that form linear channels along the c-axis. As shown in Fig. 1, the AFI crystals have a triangular lattice structure in the ab plane. The as-made AFI zeolite contains precursors in its pores. They were first burned in an atmospheric environment at 800 °C. To infiltrate Ga or Zn into the empty pores, we first immerse the platelet crystals with liquid Ga and then heat them to 80 °C while simultaneously exerting a pressure up to ~100 bar in a sealed container. For Zn, we similarly mix Zn powder with AFI crystallites and heat them to 500 °C. A similar pressure of up to ~100 bar was applied. Then, we quenched the AFI crystals containing liquid metals by immersion into liquid nitrogen. The final sample is a solid mixture of AFI crystallites embedded either in solid Ga or Zn and hereinafter referred to as Ga@AFI and Zn@AFI. Since transport measurements are not possible with such samples due to the short circuit through the metal as well as the poor contact between the metallic matrix and the nanowires, we use DC magnetization and specific heat measurements to characterize the superconducting behavior.

It is remarkable that the oxygen atoms lining the wall of the AFI channels can be the reason why liquid Ga and Zn can overcome their surface tension and penetrate into the pores of AFI crystals under moderate pressure, whereas Sn and Bi, for example, cannot. For Ga and Zn the electronegativity is 1.81 and 1.65, respectively, therefore they have a greater difference to the electronegativity of oxygen, 3.44, than Sn and Bi. From the liquid inlet pressure $P_l = \frac{4\gamma\cos\theta}{d}$, where $\gamma$ denotes the pore size, $\gamma = 720.4$ mNm$^{-1}$ is the liquid Ga metal’s surface tension in the air, and $\theta$ is the contact angle, one can estimate that $\theta$ must be very close to $\pi/2$, or the liquid would not be able to enter the pores.

**Results and discussion**

The center-to-center distance of 1.37 nm in the AFI crystallites was synthesized by the hydrothermal method [21].

**DC magnetization**

Fig. 2 shows the field-cooled (FC) and zero-field-cooled (ZFC) DC magnetization of Ga@AFI measured with a VSM SQUID magnetometer. In contrast to the observed sharp transition, the 1D nature of free-standing Ga nanowires would be expected to lead to a rather broad transition due to the phase slips. The observed sharp transition must therefore be due to the Josephson coupling between the nanowires. The ZFC data reveal the flux expulsion and subsequent flux treading as the temperature rises. The FC data show only a partial flux expulsion. The ZFC and FC data indicate that macroscopic screening currents can be formed in Ga@AFI nanowire arrays embedded in the insulating AFI crystals, which require transverse tunneling current between the Ga nanowires via the Josephson coupling.

**Specific heat**

The specific heat of Ga@AFI and Zn@AFI was measured with our dedicated home-made calorimeter [27,29]. We analyze the...
specific heat in the normal state in the standard approach: 
\[ C_n(T \rightarrow 0) = \gamma_n T + \sum_{\beta} 2kT^{2k+1}. \]
Here the first term is the electronic contribution of Ga@AFI (or Zn@AFI) with the Sommerfeld constant \( \gamma_n \). It is denoted by \( C_{\text{elect}} \) below. The second term is the low-temperature expansion of the lattice specific heat according to the Debye model. We can obtain the electronic contribution using a magnetic field strong enough to suppress superconductivity in the nanowires. The specific heat jump associated with the superconductivity will be denoted in the following by \( \Delta C \). Fig. 4 shows \( C_{\text{elect}}/T \) of Ga@AFI (Fig. 4a) and Zn@AFI (Fig. 4b). We can see the superconducting transition anomaly \( \Delta C \), which is surprisingly sharp for both samples considering the quasi-1D nature of these composites. For Ga@AFI, the transition midpoint is at 7 K, but with a fluctuation tail up to
7.7 K. For Zn@AFI, the midpoint occurs at 3.86 K. This is in good agreement with the results of the magnetization.

It is obvious that the superconducting contribution to the specific heat of the Ga nanowires is extremely low. $\Delta C$ represents only 0.3% of the total specific heat. Despite the enormous $T_c$ enhancement, these Ga nanowires in AFI zeolite are therefore not suitable for applications due to the very low filling factor of the zeolite pores. Nevertheless, it is amazing how sharp the superconducting transition is and that the composite material can still produce a significant Meissner effect.

The situation is completely different with Zn nanowire arrays. The superconducting transition anomaly $\Delta C$ of Zn@AFI represents 25% of the total specific heat of the composite material and is therefore clearly visible in the total specific heat without the need to subtract background data. This means that Zn@AFI has a very high pore filling factor, and the nanowires form a homogeneous and very dense array. The Josephson coupling between the wires is so strong that the sample remains a type I superconductor, as can be seen by the sharp peaks sitting on top of the specific heat jumps at $T_c$. This is typical for type I superconductors [30], where the superconducting transition becomes a first-order nature in any finite magnetic field. Although we have carefully tried to compensate for the residual magnetic field in our superconducting magnet cryostat, the peak does not vanish when approaching zero field, which is most likely due to the Earth’s magnetic field, which in Hong Kong is almost perpendicular to the axis of our superconducting magnet and hence cannot be compensated.

For a standard BCS superconductor, the BCS theory predicted that $\frac{\Delta C}{\gamma T_c} = 1.43$ and $\frac{\Delta H_{c1}}{\gamma T_c} = 3.53$. For Ga@AFI, from the specific heat, we obtain $\frac{\Delta C}{\gamma T_c} = 1.48$ and $\frac{\Delta H_{c1}}{\gamma T_c} = 3.6$, where $2\Delta_0$ is the full BCS superconducting gap at zero temperature. For bulk Ga, we have $\frac{\Delta C}{\gamma T_c} = 1.44$ and $\frac{\Delta H_{c1}}{\gamma T_c} = 3.52$, where $2\Delta_0$ was obtained from a fit with the single-band alpha model [31]. These results indicate that Ga@AFI is a BCS superconductor despite nanostructuring. However, the electron-phonon coupling in Ga@AFI is somewhat stronger than that of bulk Ga, as indicated by the measured $\frac{\Delta C}{\gamma T_c} = 1.48 > 1.44$, where $\frac{\gamma n T_c}{2\Delta_0} = 1.44$ is the BCS value. Similarly, for Zn@AFI, we get $\frac{\Delta C}{\gamma T_c} = 1.54$ and $\frac{\Delta H_{c1}}{\gamma T_c} = 3.6$ while for bulk Zn $\frac{\Delta C}{\gamma T_c} = 1.15$ and $\frac{\Delta H_{c1}}{\gamma T_c} = 3.2$. The superconductivity of nanostructured Zn therefore also has a BCS character. We also see that the electron-phonon coupling in Zn@AFI is slightly enhanced, as indicated by $\frac{\Delta C}{\gamma T_c} = 1.54$, which is greater than the BCS value of $\frac{\Delta C}{\gamma T_c} = 1.15$.

**Superconducting phase diagrams**

The superconducting phase diagrams for Ga@AFI and Zn@AFI are shown in Fig. 5. The diagrams are derived from the magnetization data and for Zn@AFI also from the specific heat. Ga@AFI shows the characteristic magnetization hysteresis loops of a type II superconductor. Hence, we derived the temperature dependence of the upper critical field $H_{c2}(T)$ from the onset of the Meissner signal in the $M(H)$ data, and from $M(H)$ (Fig. 5a). A fit to the standard Werthamer, Helfand and Hohenberg (WHH) model [32] was used to extrapolate the upper critical field to zero temperatures to obtain $H_{c2}(0) = 800$ mT. The model fits well with the data, except at high temperatures, where the data deviate toward higher temperatures. According to the specific heat, this is due to the fluctuation tail above the superconducting main transition at 7 K. The lower critical field $H_{c1}$ is normally obtained from the first deviation point from a linear behavior of the initial branch of the $M(H)$ hysteresis loops. This happens with very low magnetic fields of ~3 mT at 2 K, and the simple expression $H_{c2}(T)/H_{c0} = 1 - (T/T_c)^2$ from the Ginzburg-Landau theory was used to extrapolate the data to zero temperature to obtain $H_{c2}(0) = 3.2$ mT. Note that the latter $H_{c2}(0)$ determination is not very accurate and should only provide a rough estimate.

Zn@AFI could be identified as type I superconductor from the specific heat data. We determine the temperature dependence of the critical field as the upper onset of a Meissner effect in the $M(T)$ data, and from the $T_c(T)$ value in the specific heat, which was determined from the centers of the specific heat jumps that occur just above the peaks. The data agree with the expression $H_{c2}(T)/H_{c0} = 1 - (T/T_c)^2$ from the Ginzburg-Landau theory sufficiently well to determine $H_{c2}(0) = 26.4$ mT.

**Discussion**

We have observed an enormous increase in the superconducting transition temperature for both the Ga and Zn sub-
nanowires in the linear pores of AFI zeolite single crystals. While the $T_c$ enhancements are certainly caused by the confinement in the nanostucture, it is remarkable that both composites show characteristics known only from bulk materials, including a sharp superconducting transition and a distinct Meissner effect.

When the size of a conductor is reduced to the Angstrom scale, both the electron and the lattice characteristics can be greatly modified. With the support of AFI templates, Ga and Zn nanowires may form metastable states that should not be stable in the free-standing form. $T_c$ enhancements in low-dimensional superconductors are known [3–7,10,11] but are rarely as strong as what we are observing here. Several factors must be considered to explain them. Granular superconductors show enhancements in their superconducting properties [33–38], and in fact a $T_c$ enhancement of up to 6.4 K in granular Ga was reported [3]. While we believe that our nanowires are most likely of crystalline quality, the arrangement in Josephson-coupled arrays is similar to the coupled grains in granular superconductors, and therefore, similar mechanisms may apply. Various mechanisms have been proposed: it has been demonstrated that quantization of electron motion can have a beneficial effect on $T_c$ in thin superconducting layers [39] and in small isolated superconducting grains [35]. For very small Sn nanoparticles, the so-called “shell effect” caused by the discretization of energy levels was attributed to significant enhancements in the superconducting gap [40]. The importance of coupling of superconducting nanostructures in granular materials was investigated both experimentally [41] and theoretically [42], and it was shown that in weakly coupled nanograins, $T_c$ can be increased as a function of decreasing coupling strength [41]. Further mechanisms consider an increased electron-phonon coupling at the surface of nanostructures [43] or the curvature of the surface in cylindrical nanowires [44]. Finally, superconducting nanowire arrays were also considered as a realization of “superstripes”, in which the inclusion of 1D superconducting elements in superlattices was predicted to cause a strong $T_c$ improvement [45–47]. It must be pointed out that without such positive effects for the Cooper pairing, the $T_c$ of a superconductor should rather be reduced in small dimensions [14,15,48].

For our 1D sub-nanowire arrays embedded in the zeolite matrix, two further important effects have to be considered. The BCS theory [49] tells us that the transition temperature of a superconductor is determined by $k_B T_c = 1.13 \hbar \omega_D \exp(-1/N(0)V)$, where $\hbar \omega_D$ is the Debye temperature, $N(0)$ the density of state at the Fermi level, and $V$ is the electron-phonon coupling. Normally, compared with bulk metals, the free-standing metal nanowires should have a lower Debye temperature owing to the many soft modes of the thin wire. However, the Ga@AFI and Zn@AFI may have higher Debye temperatures if we consider them as a composite, in which the soft modes are suppressed by the rather rigid AFI pores. This is because AFI has a much higher Debye temperature than either Ga or Zn. It is also remarkable that a high-pressure phase of Ga with a different crystal structure reaches a $T_c$ value of 7.5 K [50], which is more or less identical to the $T_c$ value of our Ga@AFI. It is thus likely that our Ga nanowires have a crystalline structure that differs from the bulk at ambient pressure. Another effect that probably applies to our 1D Ga and Zn sub-nanowires is the existence of multiple van Hove singularities in their electronic density of states. Besides a high Debye temperature, a high electronic density of states at the Fermi energy is the second ingredient for high transition temperatures in the BCS $T_c$ formula. If the fermi level of the nanowires is at or near a van Hove singularity, their electronic density of states is significantly increased. These elements may account for the enhanced $T_c$, while it is the dense array structure with a strong Josephson coupling between the wires that prevents the occurrence of phase slips events and thus stabilizes a state of global phase coherence throughout the array. Only the latter can explain the observation of a sharp specific heat transition, a pronounced Meissner effect and the preserved type I superconductor behavior in Zn@AFI.

Our ultra-thin sub-nanowire arrays in the nanocomposite materials Ga@AFI and Zn@AFI therefore represent a promising approach for the realization of novel “bulk” superconductors with improved superconducting parameters. For Ga@AFI, this approach appears unfortunately limited by the low filling factor of the AFI pores, as the tiny specific heat anomaly demonstrates. However, Zn@AFI shows a very large superconducting transition anomaly in the specific heat, which is characteristic of a very high pore filling factor.

Conclusions

In this article, we report on the investigation of Ga nanowire and Zn nanowire arrays fabricated using AFI zeolite templates with a pore size of 0.74 nm. To our knowledge, these are the thinnest metal sub-nanowires ever produced. In both cases, we observe huge enhancements of the superconducting transition temperatures compared with the bulk values. We speculate on the source of the $T_c$ enhancement being due to the increased electronic density of states in the 1D structures with their van Hove singularities, as well

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Fig. 5. The superconducting phase diagrams of Ga@AFI (a) and Zn@AFI (b). In (a) a fit with the standard Werthamer, Helfand and Hohenberg (WHH) model for the upper critical field of a type II superconductor was added [32] and in (b) a fit with the standard Ginzburg-Landau model for the critical field of a type I superconductor.
as in the effect of the rigid AFI pore walls, which may significantly increase the Debye temperature of the metal nanowires embedded in the pores. In addition, it is likely that the crystalline structure of the 1D nanowires differs from the bulk and is more advantageous for electron-phonon coupling.

Experimental section

Fabrication of Ga@AFI and Zn@AFI

The micro-platelet AFI zeolites with linear channels were used as templates for the fabrication of Ga and Zn nanowires. We synthesized the AFI crystals using the hydrothermal method as described in detail in Reference [21]. The ingredients used were aluminum oxide, phosphorus pentoxide, silicon dioxide, and triethanolamine. The liquid Ga (or Zn) was embedded in the AFI under high pressure up to 100 bar at 80 °C (or 500 °C for Zn) in a sealed container and rapidly cooled in liquid nitrogen. Finally, we obtained Ga@AFI and Zn@AFI.

Magnetic characterization

The magnetization of Ga@AFI and Zn@AFI was measured with a commercial Quantum Design Vibrating-Sample SQUID magnetometer under ZFC and FC condition in an applied magnetic field of 20 Oe for Ga nanowires and 1 Oe for Zn nanowires. In further field sweep experiments, the temperature was set in the range from 1.8 to 7 K.

Specific-heat characterization

We have used a homemade calorimeter that can be used in both long relaxation mode and modulated temperature AC mode [29,51]. While the AC technique provides the ultra-high-resolution required to detect the tiny electronic signal of nanowires in the insulating zeolite matrix, the relaxation technique is used to determine the absolute value of heat capacity with an accuracy of 1% of the total specific heat. To remove the background signal from AFI and some bulk Ga and Zn residues on the AFI surface, a slightly higher magnetic field than the critical field value was applied, and the resulting normal state data were used to separate the non-superconducting background contribution.

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