Possible high-Tc superconductivity at 45 K in the Ge-doped cluster Mott insulator GaNb4Se8

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Abstract

The Ge-doped GaNb4Se8 polycrystalline samples were synthesized by solid-state reaction method. Zero resistance transitions were observed in one batch of samples with the highest onset superconducting Tc at 45 K. This discovery may demonstrate a new class of Nb-based high-Tc superconductors arising from doped Mott insulators.

Full Text

Possible High-Tc Superconductivity at 45 K in the Ge-Doped Cluster Mott Insulator GaNb4Se8

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Abstract

Polycrystalline samples of Ge-doped GaNb4Se8 were synthesized via solid-state reaction. Zero-resistance transitions were observed in one batch of samples, with the highest superconducting onset temperature reaching 45 K. This discovery may represent a new class of Nb-based high-temperature superconductors emerging from doped Mott insulators.

Keywords: GaNb4Se8, doping, Mott insulator, superconductivity

Introduction

In 1986, Bednorz and Müller discovered superconductivity in Ba-doped La2CuO4 with a critical temperature (Tc) of 30 K, ushering in a new era of high-temperature superconductivity research [1]. La2CuO4 exemplifies a broad family of copper oxides hosting strongly correlated electrons that form an antiferromagnetic Mott insulating state. Carrier doping into their CuO2 planes disrupts electronic correlations and gives rise to rich phase diagrams featuring high-temperature superconductivity. Building on this paradigm, subsequent work rapidly pushed Tc to 93 K in YBa2Cu3O7 and achieved a record of 135 K in HgBa2Ca2Cu3O8 that remains unbroken [2-3]. The discovery of iron-based and nickel-based superconductors in this century has further demonstrated that doping strongly correlated electron systems is a pivotal route to discovering high-temperature superconductors [4-8].

GaNb4Se8 is a well-known cubic lacunar spinel with the general formula AM4X8 (A = Al, Ga, Ge; M = V, Nb, Mo, Ta; X = chalcogen). First synthesized in 1984 by Benyaich et al. as a cluster compound [9], it features Nb4 tetramers arranged in a pyrochlore-type network, as shown in Fig. 1 [Figure 1: see original paper]. In GaNb4Se8, an unpaired electron occupies the molecular t2 orbital, forming a nonmagnetic Mott insulating ground state. The interplay of electron correlations, spin-orbit coupling, and Jahn-Teller effects produces complex physics in this material, which undergoes a cubic-to-cubic structural transition and quadrupolar ordering of molecular orbitals on Nb4 clusters at TQ = 50 K, followed by structural distortions along different directions into an orthorhombic lattice at TM = 31 K [10-15]. The formation of a valence bond solid state at low temperatures has also been proposed [15]. Under high pressure, GaNb4Se8 transforms from a Mott insulator to a metallic and superconducting state with Tc = 2.9 K at 13 GPa [16]. However, no successful carrier doping studies have been reported for GaNb4Se8 to date.

In recent years, our research has focused on synthesizing and characterizing Mo/Nb-based transition metal compounds, leading to the discovery of numerous superconducting materials. These include the quasi-one-dimensional K2Mo3As3 [17], the ternary boride Mo5GeB2 [18], the P/As-doped silicide Mo5Si3 [19-20], the gallium cluster compound Mo4Ga20As [21], the Chevrel-phase KxMo6Se8 [22], the intercalated dichalcogenide Ge-NbSe2 [23], and the binary NbS [24], among others. Here we report the possible emergence of high-temperature superconductivity in the cluster Mott insulator GaNb4Se8 induced by Ge doping.

Figure 1. Schematic crystal structure of Ge-doped GaNb4Se8, the Nb4 tetrahedron cluster, and the molecular orbital scheme of the Nb4 tetramer.

Experimental Methods

Polycrystalline samples of Ge-doped Ga1-xGexNb4Se8 were synthesized via solid-state reaction. High-purity (99.99%) Ga, Nb, Se, and Ge powders were weighed, mixed, and sealed in evacuated quartz ampules. The ampules were heated at 900 °C for 72 hours. The resulting mixtures were thoroughly reground, pressed into pellets, resealed in evacuated quartz ampules, and heated again at 1000 °C for another 72 hours. All preparation procedures were performed in a glove box filled with high-purity Ar gas (O2 and H2O content less than 0.1 ppm) to prevent contamination. The obtained samples are black and appear stable in air. We note that GeSe crystals frequently accumulate at the ends of quartz ampules due to their volatility at lower temperatures, making Ge doping at the Ga site extremely difficult and uncontrollable.

Phase characterization was performed using powder X-ray diffraction (XRD) on a PANalytical diffractometer with Cu-Kα radiation. Electrical resistance measurements were conducted using a Quantum Design physical property measurement system (PPMS) with the standard four-probe method. DC magnetization measurements were carried out using a Quantum Design magnetic property measurement system.

Results and Discussion

Among hundreds of samples prepared, only one batch from a single ampule exhibited zero-resistance transitions, though the electrical properties varied from piece to piece. The nominal composition of this batch was Ga0.9Ge0.2Nb4Se8, with excess Ge added to compensate for volatilization losses. Figure 2a [Figure 2: see original paper] shows the temperature-dependent resistance of two samples (#1 and #2) measured with an applied current of 1 mA. For these measurements, the samples were cut into irregular shapes without polishing, with dimensions of approximately 5 mm in length and cross-sectional areas of 1–2 mm^2. Sample #1 shows a superconducting transition with onset at Tc = 45 K, while sample #2 shows an onset at 40 K; both achieve zero resistance at lower temperatures. Both samples also exhibit resistivity anomalies around 60–80 K, indicating additional phase transitions.

The zero-resistance transitions are magnified in Fig. 2b [Figure 2: see original paper] and compared with three other superconductors—W5Si3-xPx, KxMo6Se8, and Ba(FeCo)2As2—demonstrating robust zero-resistance superconductivity in both samples. Notably, just below its zero-resistance transition at 34 K, sample #1 exhibits a small region of negative resistance values. This phenomenon arises from local reverse superconducting percolation paths between the voltage probes and has been occasionally observed in our superconductivity studies when samples are not single-phase. The W5Si3-xPx superconductor shows the same negative resistance behavior at 6 K. This negative resistance segment further confirms the occurrence of genuine superconductivity in sample #1.

We note that for this batch, all superconducting signals disappeared after several days of storage in a glove box, with the samples becoming insulating. These zero-resistance transitions represent the only data we have measured to demonstrate superconductivity. One possible explanation for this loss is that the Ge-doped samples are unstable and gradually decompose back into the parent compound GaNb4Se8 over time.

After the disappearance of superconducting signals, the phase composition of these samples was verified by powder XRD at ambient temperature, as shown in Fig. 3a [Figure 3: see original paper] alongside data for pure undoped GaNb4Se8. The Ga0.9Ge0.2Nb4Se8 sample contains NbSe2 and other minor impurities, with GaNb4Se8 as the main phase that is nearly identical in lattice constant to the undoped material. Figure 3b [Figure 3: see original paper] displays the temperature-dependent magnetization of the Ga0.9Ge0.2Nb4Se8 sample after losing zero resistance, measured under a field of 100 Oe; the behavior resembles that of the undoped sample reported in Ref. [12]. Figure 3c [Figure 3: see original paper] shows the temperature-dependent resistance of undoped GaNb4Se8, exhibiting typical Mott insulating behavior.

Conclusion

In summary, zero resistance was observed in Ge-doped cluster Mott insulator GaNb4Se8 with a superconducting onset temperature of 45 K. Since no other physical phenomenon has produced zero resistance at such temperatures, our discovery may represent a new class of Nb-based high-temperature superconductors.

Figure 3. (a) Powder XRD patterns of the Ga0.9Ge0.2Nb4Se8 sample and undoped GaNb4Se8. (b) Temperature dependence of magnetization for Ga0.9Ge0.2Nb4Se8 sample after the loss of zero resistance. (c) Temperature dependence of electrical resistance of undoped GaNb4Se8.

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