Superconductivity at 10.4 K in a novel quasi-one-dimensional ternary molybdenum pnictide $K_2Mo_3As_3$

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Abstract

Here we report the discovery of the first ternary molybdenum pnictide based superconductor $K_2Mo_3As_3$. Polycrystalline samples were synthesized by the conventional solid state reaction method. X-ray diffraction analysis reveals a quasi-one-dimensional hexagonal crystal structure with $(Mo_3As_3)_2^-$ linear chains separated by K$^+$ ions, similar as previously reported $K_2Cr_3As_3$, with the space group of $P-6m2$ (No. 187) and the refined lattice parameters $a = 10.145(5)$ Å and $c = 4.453(8)$ Å. Electrical resistivity, magnetic susceptibility, and heat capacity measurements exhibit bulk superconductivity with the onset $T_c$ at 10.4 K in $K_2Mo_3As_3$ which is higher than the isostructural Cr-based superconductors. Being the same group VIB transition elements and with similar structural motifs, these Cr and Mo based superconductors may share some common underlying origins for the occurrence of superconductivity and need more investigations to uncover the electron pairing within a quasi-one-dimensional chain structure.

1. Introduction

In regardless of the unclear underlying mechanism for the unconventional high-$T_c$ superconductivity in cuprates and iron pnictides/chalcogenides, the occurrence of superconductivity is strongly related to the existence of some certain structural motifs as CuO$_2$ planes or Fe$_2$As$_2$/Fe$_2$Se$_2$ layers in varied crystal structures, which actually has been the guidance for searching new superconductors in these materials [1–10]. Back to the early 1970s, there were a large number of molybdenum chalcogenide superconductors $A_2Mo_6X_6$ were discovered, and some of them are superconducting with quasi-one-dimensional (Q1D) features [22–26]. These Chevrel phase superconductors were regarded as remarkable high temperature superconductors due to their high $T_c$ and high upper critical field and attracted intensive research interests in those years (for PbMo$_6S_8$, $T_c \sim 15$ K, $H_{c2} \sim 60$ T) [13,27]. Some of them exhibit more exotic physical phenomena such as the reentrant superconducting phase, the coexistence of superconductivity with long-range ferromagnetic order in HoMo$_6S_8$, and the unique magnetic field induced superconductivity in Eu$_2$Ho$_{0.75}$Sn$_{0.25}$Mo$_6S_7.2$Se$_{0.8}$ [14,20]. However, the study on these superconductors was almost broken off by the later discovery of high-$T_c$ cuprates and iron-based superconductors in spite of many fundamental problems are still under debate [21].

Recently, a novel family of chromium arsenide based Q1D superconductors $A_2Cr_3As_3$ ($A$ = alkali metal) were reported, which shares the same $(Cr_3As_3)^2^-$ chain-like structural motif just as the $(Mo_3X_6)^2^-$ [28–31]. These Cr-233 superconductors crystallize in a monoclinic structure with a simple unit cell containing six formula units. Strong electron correlations and magnetic fluctuations, highly anisotropic upper critical field exceeding the Pauli-pair breaking limit, line nodes in the superconducting gap, and Tomonaga-Luttinger liquid behavior were observed by different experimental techniques and showed the possibility of unconventional superconductivity [28–45]. Spin-triplet electron pairing was proposed in these Cr-233 superconductors from the beginning but a consensus is still far to be concluded [28–38,42,43,46]. And lately, superconductivity was also found in...
the Q1D-type ACr3As3 crystals which actually have identical crystal lattice to the Mo-based M2Mo6X6 [22,47–50]. These 133-type Cr-based superconductors exhibit similar high upper critical field and strong electron correlations within a centrosymmetric lattice, but negative chemical pressure effect on Tc from the replacement of alkali metal cations which is opposite to that of the Cr-233 superconductors, and more investigations are still ongoing to further understand their physical characteristics [28–31,49,50].

As the elements Cr and Mo belong to the same group VIB transition metals with similar electronic configuration, a question arising is whether these two families of superconductors share some common underlying origins for the occurrence of superconductivity. In this manuscript, we report the successful synthesis of a Q1D compound K2Mo3As3 that has the same crystal structure as the Cr-233 superconductors. This Mo-233 type K2Mo3As3 shows bulk superconductivity at a higher Tc of 10.4 K, which may shed new lights on the understanding of the superconducting orders in these group VIB transition metal compounds.

2. Experimental

Polycrystalline K2Mo3As3 samples were synthesized by the conventional solid state reaction method in two steps, using elemental K pieces (99%), Mo powder (99.95%) and As powder (99.999%) as the starting materials. At first, the mixtures of K, Mo and As elements with the atomic ratio of 2.5:3:3 were placed in an alumina crucible, covered by an alumina cap and then sealed in an evacuated quartz tube (C24 10 4 Pa). The sealed quartz tube was slowly heated to 523 K and kept for 20 h in a muffle furnace, and then cooled down to room temperature. After the initial reaction, the mixture of these intermediate products could be thoroughly ground into fine powders, which were then pressed into small pellets. Secondly, the pellets were placed into an alumina crucible, and sealed into a Ta tube with arc welding in argon atmosphere (~0.05 MPa). The Ta tube was sealed in an evacuated quartz tube, and then it was slowly heated to 1,123 K and sintered for 50 h in the muffle furnace before cooled down to room temperature by furnace shut-down. The preparation procedures were strictly carried out in a glove box filled with high-purity Ar gas (O2 and H2O content less than 0.1 ppm) to avoid any possible contamination by oxygen or moisture to the samples. Due to the easy volatilization of alkali metals and arsenic, to obtain single phase samples with no obvious binary impurities, we did many attempts for the optimization of the synthesizing conditions and the ratio of starting materials since no ternary chemical phase of alkali metal molybdenum arsenide has ever been reported.

The obtained K2Mo3As3 samples are black in color and extremely reactive in air. Hence any exposure to air should be avoided when performing measurements on these samples. Needle-like tiny crystals are occasionally observed on the as-grown sample surface. The crystal structure was characterized at room temperature by powder X-ray diffraction (XRD) using a PAN-analytical X-ray diffractometer with Cu-Kα radiation. The sample morphology was characterized with a Phenom scanning electron microscope (SEM). The electrical resistivity and heat capacity measurements were performed on a Quantum Design physical property measurement system with the standard four-probe method and thermal relaxation method, respectively. The dc magnetization was measured with a Quantum Design magnetic property measurement system.

3. Results and discussion

The crystal structure of K2Mo3As3 is determined by the powder XRD analysis, which reveals identical lattice symmetry with that of previously reported Q1D noncentrosymmetric K2Cr3As3-type superconductors [28]. In Fig. 1a the crystal structure is depicted

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Fig. 1. (Color online) Crystal structure and morphology. (a) The schematic crystal structure for the M6X8 cluster, the M3X3 chain, and the K2Mo3As3 lattice. (b) The SEM morphology characterization for the fresh fracture surface of the K2Mo3As3 polycrystalline sample. (c) The powder XRD patterns and structural refinement for K2Mo3As3.
with the schematic M₆X₆ cluster and the M₆X₃ chain condensed from the cluster. The K₂Mo₃As₃ can be considered as linear hexagonally arranged (Mo₃As₃)²⁻ chains separated by the K⁺ alkali cations that act as a charge reservoir. The SEM morphology characterizations for the fresh fracture surface of the as-grown sample show all needle-like crystal grains and explicitly manifest the Q1D lattice structure, as displayed in Fig. 1b. The XRD analysis was performed on powdered samples and the typical diffraction pattern with 2θ from 5° to 90° is shown in Fig. 1c. All the reflection peaks can be well indexed by the hexagonal lattice structure of the space group P-6/m (No. 187) with no impurity phase observed, and the refined lattice parameters are a = 10.145(5) Å and c = 4.453(8) Å. We note that due to the superior ductility for K₂Mo₃As₃ and the highly orientation of the needle-like crystal grains, the intensity for the diffraction peaks is not well refined. Hence we have not obtained the detailed atomic coordinates from the diffraction data. Comparing with that of the isostructural K₂Cr₃As₃, the crystal lattices expand more evidently along c-axis (~5.3%) than a-axis (~1.6%) due to the replacement of transition metals, which is quite different with the replacement of alkali metals in the K₂Cr₃As₃ series that mainly alters the a-axis parameter or the inter-chain distance [28–31]. This suggests that the Q1D chain structure is dominated by the transition metal elements bonded with arsenic, while the inter-chain bonding is much weaker. Here we note that the excess using of elemental K in the starting materials is important to obtain single-phase sample, otherwise lots of binary impurities would be observed in the sintered sample.

As we measured the low temperature resistivity for K₂Mo₃As₃, superconducting transitions were observed in all batches of samples. In Fig. 2a we show the temperature dependence of electrical resistivity for three typical samples of K₂Mo₃As₃ from 1.8 to 300 K under zero fields. The electrical resistivity ρ(T) usually exhibits metallic characteristic in the normal state while semiconducting behavior sometimes appears at low temperature in some batches of samples. High quality single crystal is necessary to clarify the normal state electrical transport characteristics. All samples exhibit unambiguous superconducting transitions near the similar onset critical temperature of Tᶜ ~10.4 K with zero resistance appeared at low temperature, and the typical superconducting transition width is about 0.3 K as shown in the inset for sample A. The Tᶜ in this Q1D type K₂Mo₃As₃ compound remarkably exceeds that of all other previously reported Q1D superconductors [22,24,25,28–31,49–53]. To characterize the upper critical field μ₀Hc₂, the electrical resistivity from 2 to 12 K with temperature sweeping was measured for sample A under a constant magnetic field with the direction perpendicular to the electrical current, the fields were varied from 0 to 16 T with 1 T interval, and the data are shown in the inset of Fig. 2b. Upon applying magnetic field, Tᶜ shifts to lower temperature sharply at first, and then it becomes slowly and the superconducting transition width shows a broadening effect similar as Tₐ₂Mo₆Se₆ [24]. In the normal state, no obvious magnetoresistance effect appears. Fig. 2b represents the temperature dependence of μ₀Hc₂ and the data show a slowly increase of the absolute value for the dHc₂/dT when temperature decreases. The data are fitted with the Ginzburg-Landau formula, Hc₂(T) = Hc₂(0)[(1−t²)/(1+t²)], in which t = T/Tc. The zero-temperature upper critical field μ₀Hc₂(0) is estimated to be 22.0 T, which is just above the Pauli paramagnetic limited critical field μ₀Hₚ = 1.84Tₑ₉ = 19.1 T [54]. Moreover, the behavior of the dHc₂/dT does not exhibit obvious Pauli pair breaking effect under the measured fields, which may indicate possible unconventional superconductivity in K₂Mo₃As₃.

To demonstrate the bulk superconductivity in K₂Mo₃As₃, the temperature dependence of dc susceptibility and heat capacity were measured and shown in Fig. 3. In Fig. 3a we show the susceptibility data for the above-mentioned three samples from 2 to 12 K with zero-field-cooling (ZFC) and field-cooling (FC) modes under a stable magnetic field of 10 Oe. Both ZFC and FC data show clear diamagnetic superconducting transitions below 10.2 K, which is consistent with the electrical resistivity measurements. The diamagnetic shielding volume fraction derived from the ZFC data is close to 100% at 2 K, suggesting the bulk superconductivity in K₂Mo₃As₃. The isothermal magnetization measurement at T = 2 K for sample A exhibits typical type-II superconductivity as shown in Fig. 3b. The high-temperature susceptibility χ(T) follows Curie-Weiss behavior with no magnetic order appearing. The temperature dependence of heat capacity for sample A is shown as the relationship of Cₚ/T vs T² in Fig. 3c with a clear superconducting transition. The normal state data are linearly fitted with both electron and phonon contributions by Cₚ/T = γ + βT². From the fitted parameters we get the Sommerfeld coefficient γ as 13 mJ mol⁻¹ K⁻² which indicates much weakened electron correlations than Cr-233 superconductors [28–31], and the Debye temperature θₑ as 234 K calculated from θₑ = (12/5)NRπ⁴/β¹⁻³. The temperature dependence of electron contributions for heat capacity is normalized as (C–Cₚh)/(γ/T) vs. T and shown in Fig. 3d (where Cₚh is the phonon contribution of βT²), which exhibits the characteristic heat capacity jump (∆C) for the superconducting transition. The dimensionless heat capacity jump ∆C/T at Tc is about 1.54, which confirms the bulk superconductivity in K₂Mo₃As₃. We note that the value of ∆C/T is smaller for sample C, which might be due to possible variation of sample stoichiometry that affects the occurrence of superconductivity severely.
In conclusion, we successfully synthesized a MoAs-based ternary compound K$_2$Mo$_3$As$_3$ which has a typical Q1D crystal structure by the conventional solid state reaction method. Electrical resistivity, dc magnetization, and heat capacity measurements revealed the existence of bulk superconductivity in K$_2$Mo$_3$As$_3$ with an onset $T_c$ of 10.4 K. This discovery provides the first MoAs-based superconductor and may help to uncover more insights into the deep physics of Cr and Mo based Chevrel phases.

Note added: the isostuctural Rb$_2$Mo$_3$As$_3$ and Cs$_2$Mo$_3$As$_3$ were also synthesized with superconductivity observed at 10.6 and 11.5 K, respectively.

Conflict of interest

The authors declare that they have no conflict of interest.

Acknowledgments

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