Competition of superconductivity and charge density wave order in Na$_x$TaS$_2$ single crystals

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Abstract

A series of crystals of Na$_x$TaS$_2$ with different superconducting transition temperatures ($T_c$) ranging from 2.0–4.4 K were obtained by flux method. The structural data deduced from X-ray diffraction pattern shows that the sample has the same structure as 2H-TaS$_2$. Compared with the resistivity curve of un-intercalated sample 2H-TaS$_2$ ($T_c = 0.8$ K, $T_{CDW} = 70$ K), no signal of charge density wave (CDW) was observed in our present samples Na$_{0.1}$TaS$_2$. It is thus concluded that there is a competition between the superconductivity and the CDW. With the increase of sodium content, the rise of $T_c$ in Na$_x$TaS$_2$ is caused mainly by the suppression to the CDW in 2H-TaS$_2$, and the conventional rigid band model for layered dichalcogenide may be inadequate to explain the changes induced by the slight intercalation of sodium in 2H-TaS$_2$.

Keywords: Crystal growth; Dichalcogenides; CDW; Superconductivity; Competition

1. Introduction

Layered transition-metal dichalcogenides (TMDC’s) of the type MX$_2$ (M is the transition metal, X = S, Se, Te) have been extensively studied for their rich electronic properties due to low dimensionality. Each layer of TMDC’s consists of a hexagonal transition metal sheet sandwiched by two similar chalcogen sheets, the interaction between the MX$_2$ layers is weak and van der Waals-like. Charge density wave (CDW) and superconductivity (SC) coexist in this kind of materials. The electron–phonon coupling and its relationship with the CDW are investigated by angle resolved photoemission in 2H-TaSe$_2$ and 2H-NbSe$_2$ systems [1]. It is found that the CDW transition temperature decreases and meanwhile the superconducting critical temperature ($T_c$) increases from TaSe$_2$ through TaS$_2$ and NbSe$_2$ to NbS$_2$, which indicates that these two orders (CDW and superconductivity) compete each other [2,3].

Intercalation of atoms and molecules into the weak coupled region between the MX$_2$ layers leads to significant modification of properties, which is another highlight to study TMDC’s. A variety of atoms and molecules were reported to be intercalated into the interlayer regions between the MX$_2$ layers, and the resulting compounds are superconducting [4]. Furthermore, different superconducting transition temperatures $T_c$ were found depending on the intercalated ions [5,6], and the $T_c$ increased when the intercalated TMDC’s were further hydrated. The change of properties induced by intercalation may be explained in terms of charge transfer from the intercalated atoms or molecules to the host MX$_2$ layers, the band structure is unaltered upon intercalation, and density of states (DOS) at Fermi surface (FS) changes to reflect the transfer of charges from the intercalated atoms or molecules.

In recent years, however, some experiments and calculations revealed that the change of properties of the intercalated MX$_2$ cannot be understood based on the rigid-band model. The electrical measurement of TaS$_2$(pyridine)$_{1/2}$ showed that there was no signal of CDW in the resistivity curve, which was attributed to the suppression of a structural instability by intercalation [7]. Angle-resolved photoemission was used to study the electronic band structures before and after the alkaline metal Cs and Na were intercalated into the 2H-TaSe$_2$ and VSe$_2$ [8–10], and it was found that the changes induced by intercalation...
was more extensive than that expected by the rigid-band model. Therefore, it remains controversial whether it is possible to use the rigid-band model to explain the changes induced by the intercalation in TMDC’s. In order to unravel this puzzle, more efforts are desired. In the family of TMDC’s, the sample TaS$_2$ may be one of the model systems to tackle this problem. Two basic structures of TaS$_2$ were found and defined by the different orientation of stacking chalcogen sheets, one is 1T-TaS$_2$ with Ta in octahedral coordination with $S$ atoms, another is 2H-TaS$_2$ with Ta in trigonal-prismatic coordination with $S$ atoms (L.F. [11,12]). The system 1T-TaS$_2$ shows four CDW phase transitions accompanied by changes in lattice parameters and resistivity when temperature decreases, the CDW formation could be explained by the Fermi surface nesting (L.F. [11]. However, the system 2H-TaS$_2$ is known for the existence of coordination with H$_2$TaS$_2$, 0.8 K (L.F. [11]. When sodium ions are intercalated into CDW order below 70 K and becoming a superconductor at $T_c$ below 4.7 K.

TaS$_2$ single crystal and sharp superconducting transitions showed that the crystals have the typical structure of 2H-TaS$_2$ (2H) with different superconducting transition temperatures. Measurements of X-ray diffraction and superconducting transition revealed good quality of these crystals.

2. Experiment

A traditional way for fabricating intercalated layered dichalcogen compounds consists of two steps, the first step is to prepare poly-crystalline compound or single crystal of MX$_2$ by chemical reaction or iodine-transport reaction, then the intercalation is carried out by chemical treatments, the samples are dipped into concentrated solutions containing the intercalated atoms. In this paper, we report the growth of crystals of Na$_x$TaS$_2$ (2H) with different superconducting transition temperatures. Measurements of X-ray diffraction and superconducting transition revealed good quality of these crystals.

Diffraction pattern was performed on these crystals at room temperature employing a M18AHF X-ray diffractometer (MAC Science). Crystallographic orientation and index are determined by Power-X, a program for processing X-ray diffraction data. The magnetic and transport measurements were carried out with an Oxford multi-parameter measurement system (Maglab-Exa-12). The microscopic and concentration analysis is achieved with Energy Dispersive X-ray Microanalysis (EDX) of scanning electron microscope (Oxford).

3. Results and discussion

3.1. Upper critical field and anisotropy

To our knowledge, the upper critical field $H_{c2}(0)$ of Na$_x$TaS$_2$ was rarely reported. We studied $H_{c2}(0)$ of one piece crystal of Na$_{0.33}$TaS$_2$ with $T_c$ = 4.3 K through transport measurement.

In order to determine the upper critical field and the anisotropy of superconductivity, we measured the resistive transitions at different magnetic fields with the filed direction along ab-plane (Fig. 2(a)) and c-axis (Fig. 2(b)). An sharp superconducting transition occurs at 4.83 K when the field is zero, zero resistivity is obtained at about 4.3 K. The sharp transition with width less than 0.5 K indicates the good quality of the crystal Na$_{0.33}$TaS$_2$. One can see that the resistive curve shifts parallel down to lower temperatures with the increase of magnetic field. From the mid-point of the transition curves, we determine the upper critical fields for both directions, which are shown in Fig. 3. In the Ginzburg–Landau theory, it is known that $H_{c2} = \Phi_0/2\pi \xi^2$ and $\xi \propto \sqrt{(1+r^2)/(1-r^2)}$, with $\Phi_0$, the flux quanta, $\xi$ the coherence length, $t = T/T_c$, the reduced temperature, thus one
We use above equation to fit our data and show them as the solid and dashed lines in Fig. 3. The zero temperature upper critical fields \( H_{c2}(0) \) determined in this way are \( H_{c2}(0) = 2.5T \) and \( H_{c2}^{ab}(0) = 16T \), therefore, the anisotropy \( H_{c2}^{ab}(0)/H_{c2}(0) = \xi_{ab}(0)/\xi_{c}(0) = \sqrt{m_c/m_{ab}} = 6.4 \), which is quite close to that of optimally doped YBa\(_2\)Cu\(_3\)O\(_7\). This is to our surprise since the sample here is clearly of thin-platelet shape, which looks like the much more anisotropic cuprate system Bi\(_2\)Sr\(_2\)CaCu\(_2\)O\(_8\) single crystals. In pyridine intercalated systems, the anisotropy of DC resistivity is in the order of \( 10^5 \) along \( c \)-axis and \( ab \)-plane. This extremely high anisotropy is far beyond the value we can expect in our present system. Therefore, intercalating sodium here may enhance the electrical conduction along \( c \)-axis and suppress the feature of two-dimensionality. Actually the zero temperature value of upper critical field can also be determined through the Werthamer–Helfand–Hohenberg (WHH) formula:

\[
H_{c2}(0) = K_0 \left( \frac{dH_{c2}}{dT} \right)_{T=T_c}
\]

Here, \( dH_{c2}/dT \) is the slope of \( H_{c2}(T) \) near \( T_c \), which is about 0.7163 T/K for \( H_{c2}^{c} \) and 4.5 T/K for \( H_{c2}^{ab} \). Using above formula the zero temperature values of upper critical fields are \( H_{c2}(0) = 2.13T \) and \( H_{c2}^{ab}(0) = 13.4T \), which are close to the values determined in fitting the data to Eq. (1).

### 3.2. Competition between CDW and superconductivity

Trigonal prismatic layer compound 2\( H \)-TaS\(_2\) generally exhibits a charge-density-wave related phase transition accompanied by a drop in resistivity around 70 K [7]. We thus measured the resistivity of crystals of Na\(_{0.1}\)TaS\(_2\) from 2–300 K. It is found that the resistivity \( \rho \) decreases with the temperature smoothly and the superconducting transition happens at 4.4 K, no sudden drop of resistance on the resistivity curve was observed in whole temperature region. Fig. 4 shows the comparison of resistivity between undoped 2\( H \)-TaS\(_2\) and our sample Na\(_{0.1}\)TaS\(_2\). From here it is tempting to conclude that the CDW is completely suppressed in our samples.

Fig. 2. The superconducting transition measured at different magnetic fields when the field is applied (a) perpendicular to and (b) parallel to \( c \)-axis. From the mid-point of the resistive curve one can determine the upper critical field \( H_{c2}(T) \).

\[
H_{c2}(T) = \frac{H_{c2}(0)}{1 + T^2}
\]

Fig. 3. The upper critical field determined from the mid-point of the transition curve. The solid and dashed lines here are theoretical curves of \( H_{c2}(T) = H_{c2}(0)(1 - T^2)(1 + T^2) \) with \( H_{c2}^{c}(0) = 2.5T \) and \( H_{c2}^{ab}(0) = 16T \).

Fig. 4. Comparison of resistivity between 2\( H \)-TaS\(_2\) and Na\(_{0.1}\)TaS\(_2\). For clarity, here we show only the data from 2 to 90 K. Resistivity of 2\( H \)-TaS\(_2\) is adopted from [7].
This result provides convincing evidence that there is a competition between the superconductivity and charge density wave in layered chalcogenide Na$_x$TaS$_2$ [13]. When sodium ions are intercalated into 2H-TaS$_2$, CDW order is destroyed and $T_c$ increases. The suppression to the CDW may be understood by the better c-axis conduction after the sodium intercalation. In this case the system deviates from two dimensionality as in 2H-TaS$_2$ and thus prevents the lattice instability. This is partially supported by the relatively small anisotropy of $m_c/m_{ab}$ as determined above in the sodium-intercalated samples. When the CDW is suppressed, the effective DOS at the Fermi surface is eventually enhanced leading to a much higher $T_c$.

4. Conclusion

A new way to grow crystals of Na$_x$TaS$_2$ is presented. A series of crystals with different superconducting transition temperatures $T_c$ ranging from 2.0 to 4.4 K were obtained. Compared with the resistivity curve of 2H-TaS$_2$($T_c$ = 0.8 K, $T_{CDW}$ ≈ 70 K), no signal of charge density wave (CDW) was observed in our present samples Na$_{0.1}$TaS$_2$. The upper critical field and its anisotropy (about 6.4) have also been determined. It is concluded that there is a competition between the superconductivity and the CDW order: The rise of $T_c$ in Na$_x$TaS$_2$ by increasing the sodium content may be caused by the increase of DOS at Fermi surface when the CDW is suppressed by probably a better c-axis electrical conduction.

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