Comparative Study between 2H-NbSe$_2$ and 2H-TaSe$_2$: Superconductivity and Charge Density Wave

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Abstract: Here we have compared two transition-metal dichalcogenide single crystal compounds of 2H-NbSe$_2$ and 2H-TaSe$_2$. Both the compounds show superconductivity (SC) and charge density wave (CDW) states. The change in transition temperature is related to the density of states due to the different size of transition-metal atom which does not affect significantly to their structural symmetry. This is explained qualitatively and quantitatively by the equation used for coexistence of SC and CDW state.

1. Introduction

The transition-metal dichalcogenide compounds (TMDC's) have attracted considerable interest to scientific community due to number of viewpoints including intercalation, charge-density wave, superconductivity and optical and transport properties. TMDC's are made up of X-M-X slabs generally written as MX$_2$ where M refers to transition metal atom and X chalcogen atom exhibits strong intralayer covalent bonding and weak inter-layer verder Waals bonding. Besides this the sheet of M-atoms strongly bonded and sandwiched between two hexagonal closed packed of X-layers to form either trigonal or octahedral coordination of M-atom. Then multiple MX$_2$ slabs are weakly bonded by vender Waal's bond and stacked along the direction perpendicular to layers.

2H-NbSe$_2$ shows the existence of superconductivity state at T_s = 7.4K below a Charge Density Wave (CDW) state at T_c =35K [1-3]. The evidence of CDW is reported through Neutron scattering, Scanning tunneling microscope and NMR [4-6]. In Neutron scattering experiment, an incommensurate CDW (ICDW) state

is observed below 35K associated with a wave vector q = $(1-\delta)a^*/3$ whose incommensurability 'δ' decreases from 0.025 at 33K to 0.011 at 5K. Besides this the suppression of CDW state is noticed with decreasing residual resistance ratio (RRR) without affecting the superconductivity (SC) transition temperature found on two different single crystals of $2H\text{-}NbSe_2$ grown by CVT method [2].

$2H\text{-}TaSe_2$ also shows superconductivity and charge density wave at T_s = 0.2mK and T_c =122K respectively [3, 7]. The electron and neutron diffraction experiments indicate that the ICDW appears below 122K with a wave vector q = $(1-\delta)a^*/3$ where incommensurability 'δ' is equal to 0.02 [4, 8]. This incommensurability shows stable in most of the crystals and suddenly drops to zero at 90K where $2H\text{-}TaSe_2$ becomes commensurate CDW (CCDW) state with wave vector q =$a^*/3$. The variation in CCDW transition temperature between 90K and 122K from compound to compound is not well understood yet.

2. 2H-Polytype in TMDC's

Though the different types of polytype structure have been observed in TMDC's, here we have discussed only about the intrapolytpe of *2H*-symmetry. First of all we consider a parent disordered hypothetical structure of MX_2 as shown in fig.1(a) for all the ordered *2H*-MX_2 polytypes as shown in fig.1(b), (c) & (d). This structure, which has hexagonal symmetry, will be denoted by *P* known as primitive hexagonal cell contains statistically disordered atoms of M and X with a fractional occupancy $x_M = x_X =1/3$ per MX_2. Therefore, M atoms occupy statistically the positions 1(b): 0 0 1/2 and 2(d): 01/3 2/3 1/2 whereas X atoms are disordered over the Wyckoff positions 2(e): 0 0 z and 4(h): 1/3 2/3 z with z close to $z_0 =1/4$. Thereafter the ordering mechanism for MX_2 is described in order of increasing complexity.

There are three possible different types of two MX_2 layers per unit cell are known and denoted by *2Ha*, *2Hb* and *2Hc*. The *2Ha* and *2Hc* polytype are found stabilize in Nb(Ta) dichalcogenides and Mo(W) dichalcogenides respectively. But *2Hb* polytypes are obtained for the nonstoichiometric compounds of $Nb_{1+x}Se_2$ and $Ta_{1+x}Se_2$ having excess metal atoms in the vender Waal's interlayer gap. In all the polytypes, the c-axis lattice constant is doubled with respect to primitive cell corresponding to one 2(e) and one 4(h) position for the M-atoms. Then X-positions of the primitive cell split into two 2(e) and two 4(h) positions.

Further ordering mechanism provides the difference between *2H*-polytypes as discussed below,

2Ha-polytype: The M-atoms occupy the 2(e) position whereas X-atoms fill the two 4(h) positions one each. The resulting structure has $P6_3/mmc$ symmetry. The corresponding stacking sequence is AbACbC.

2Hb-polytype: The 2(e) position is half filled and 4(h) position is filled by one quarter with M-atoms. The X-atoms occupy half of the two 4(h) position, one each. The parent hexagonal symmetry is reduced to $P\bar{6}m2$. The stacking sequence is AbACaC.

2Hc-polytype: The half of the 4(h) position is filled by M-atoms one each whereas X-atoms occupy half of the two 4(h) position, one each. The space-group type is $P6_3/mmc$ as *2Ha*-polytype. The stacking sequence is CaCAcA.
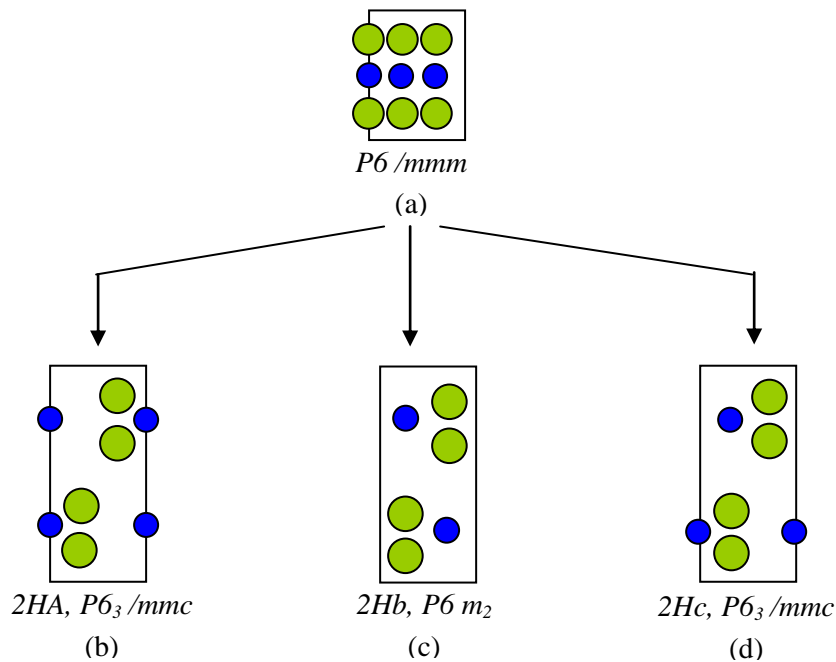

Fig. 1: Sections through the $11\bar{2}0$ plane of MX₂ and three possible models for 2H-MX₂, (a) shows disordered hypothetical structure of MX₂ and (b), (c), (d) shows possibility of 2H-polytypes. The big circles are for chalcogen atoms and small circles for transition-metal atoms.

3. Results and Discussion

Here, we have presented only the resistivity data measured along the ab-plane on two single crystals of 2H-NbSe$_2$ and TaSe$_2$ by a four-probe method from 4 to 300K.

2H-NbSe$_2$: The structure as well as the dimension of the unit cell for NbSe$_2$ is determined, from room temperature x-ray diffraction, hexagonal symmetry with lattice constant a = 3.445Å and c = 12.551Å, which has the crystallographic parameter c/a = 1.82. The temperature dependence resistivity of 2H-NbSe$_2$ is shown in fig. 2(a) and its purity is calculated ~ 66.7 from the residual resistance ratio (RRR) defined by ρ_{300}/ρ_{T_s}, where 'ρ_{T_s}' is the resistivity at superconducting transition temperature 'T_s'. From fig. 2(a), it clearly shows that the superconducting state evolves below 7.4K followed by a CDW state (visible as a small bump) around 35K similar to the previously reported results. The very poor room temperature resistivity ~ $6.8 \times 10^{-5} \Omega - cm$ defines it well inside the metallic group.

2H-TaSe$_2$: The same crystal structure of hexagonal symmetry with slight difference in dimension of the unit cell is reported for 2H-TaSe$_2$ i.e. a = 3.436Å and c = 12.696Å compare to 2H-NbSe$_2$ [9]. This provides the crystallographic parameter c/a = 1.85 close to 2H-NbSe$_2$. Its temperature dependence resistivity is shown in fig. 2(b) having purity ~ 187 [3]. The superconducting state is not seen clearly in resistivity data because it is very close to 0K and its existence is verified by magnetization which followed by CCDW and ICDW state around 90K and 122K respectively. The room temperature resistivity is ~ $1.3 \times 10^{-4} \Omega - cm$.
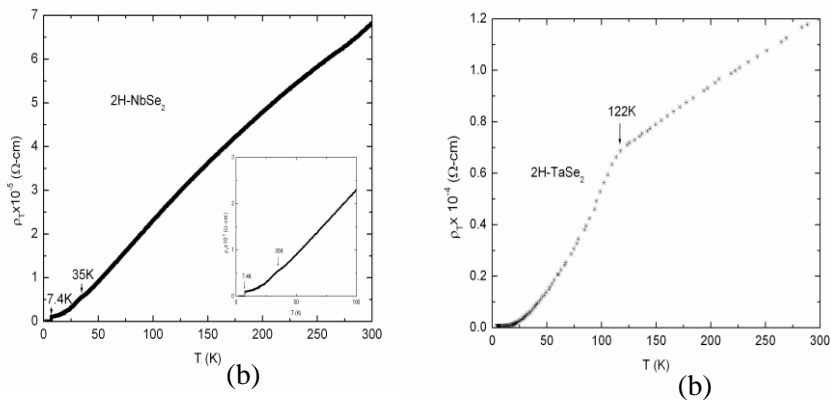

Fig. 2: Temperature dependence resistivity of (a) 2H-NbSe$_2$ [1] and (b) 2H-TaSe$_2$ [3].

In combination with trigonal coordination, both the compounds show common properties of SC and ICDW states with approximately same crystallographic parameter related to size of the cations. Then relation between onset transition temperatures of SC and ICDW states at constant normal state density of states is defined as given below [10].

$$T_s = \frac{1.13\hbar\omega_s}{k_B}\left\{1 + \frac{V_c}{V_s}\left(1 - \frac{k_B T_c}{1.14\hbar\omega_c}\right)\right\}$$ (1)

Here, $\hbar\omega_s$ ($\hbar\omega_c$) and V_s (V_c) are the phonon energy and effective interaction for SC (CDW) state respectively. The above analytical expression is equivalent to a straight-line expression i.e. $y = mx + c$ having slope $m \approx V_c\hbar\omega_s/V_s\hbar\omega_c$ with a negative sign and intercept constant $c = (1.13\hbar\omega_s/k_B)(1 + V_c/V_s)$. This analytical expression makes correlation between SC and ICDW states and explains their variation qualitatively and quantitatively for constant ratio of V_c/V_s and $V_c\hbar\omega_s/V_s\hbar\omega_c$ for a particular compound. Further, any one quantity out of transition temperature, phonon energy and effective interaction for stable SC state can be calculated from this expression if two quantities for SC and all quantities for CDW state are known and vice versa. We have also calculated $m \approx 0.09$ and $c \approx 10.21$ for 2H-NbSe₂ using the pressure effect data of *C. W. Chu* et al. [10, 11]. Regardless of the unit cell size difference between 2H-NbSe₂ and 2H-TaSe₂, the existence of SC and ICDW in 2H-TaSe₂ are well defined by equation (1) with the values of $m \approx 0.09$ and $c \approx 10.21$.

4. Conclusion

In the present study, we have noticed the increase in separation between two transition temperatures associated with SC and ICDW states in 2H-TaSe₂ compare to 2H-NbSe₂ is related to the size of transition metal atom taken from same group in the periodic table. The increase in size of metal atom increases the volume of unit cell as presented above along with the electron density of state in 2H-TaSe₂ is almost doubled compare to 2H-NbSe₂ [3]. Within this circumstance, the change in transition temperatures related to density of states in 2H-TaSe₂ is explained by the equation (1) qualitatively and quantitatively at $V_c\hbar\omega_s/V_s\hbar\omega_c \approx 0.09$ and $V_c/V_s \approx 0.37$ as found in 2H-NbSe₂. This implies that the values of $\hbar\omega_s$, $\hbar\omega_c$, V_s and V_c in 2H-TaSe₂ are changed in such a way that $V_c\hbar\omega_s/V_s\hbar\omega_c$ and V_c/V_s remains same as 2H-NbSe₂ and causes to shift

the CS state towards lower temperature and CDW state towards higher temperature in 2H-TaSe$_2$.

Acknowledgement

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