

LETTER

Structural, electrical, and thermoelectric properties of distorted $1\text{T-Ta}_{1-x}\text{Nb}_x\text{Te}_2$ single crystals

To cite this article: Y. Liu *et al* 2015 *EPL* **109** 17003

View the [article online](#) for updates and enhancements.

You may also like

- [Fano-like anti-resonances in strongly coupled binary Coulomb systems](#)
L. Silvestri, G. J. Kalman, Z. Donkó et al.
- [Interfacial-scattering-induced enhancement of the anomalous Hall effect in uniform Fe nanocluster-assembled films](#)
J. B. Wang, W. B. Mi, L. S. Wang et al.
- [The third virial coefficient of a two-component unitary Fermi gas across an Efimov-effect threshold](#)
Chao Gao, Shimpei Endo and Yvan Castin

Structural, electrical, and thermoelectric properties of distorted 1T-Ta_{1-x}Nb_xTe₂ single crystals

Y. LIU¹, W. J. LU^{1(a)}, D. F. SHAO¹, L. ZU¹, X. C. KAN¹, W. H. SONG² and Y. P. SUN^{1,2,3(b)}

¹ Key Laboratory of Materials Physics, Institute of Solid State Physics, Chinese Academy of Sciences Hefei 230031, PRC

² High Magnetic Field Laboratory, Chinese Academy of Sciences - Hefei 230031, PRC

³ Collaborative Innovation Centre of Advanced Microstructures, Nanjing University - Nanjing 210093, PRC

received 20 October 2014; accepted in final form 18 December 2014

published online 19 January 2015

PACS 74.70.-b – Superconducting materials other than cuprates

PACS 74.25.F- – Transport properties

PACS 74.62.Dh – Effects of crystal defects, doping and substitution

Abstract – A series of isovalent Nb-substituted Ta_{1-x}Nb_xTe₂ ($0 \leq x \leq 1$) single crystals, which crystallizes in a monoclinically distorted CdI₂-type structure with the $C2/m$ space group, were grown by the chemical-vapor-transport (CVT) method. For TaTe₂ ($x = 0$), a first-order transition at ~ 178 K is observed by heat capacity (C_p) measurement, accompanying with an anomaly in electrical resistivity (ρ), Hall resistivity (R_H), and especially, the sign change of thermoelectric power (S), implying the multi-band transport. This transition can be gradually suppressed by isovalent Nb substitution and disappears as $x \geq 0.2$, and correspondingly, an enhancement of electronic density of states (DOS) near the Fermi level is obtained. In addition, the local Ta-Te/Ta-Ta bonding instability may play an important role for the structural phase transition of TaTe₂.

Copyright © EPLA, 2015

Introduction. – Layered transition metal dichalcogenides (TMDs) have been studied for several decades due to their rich structural chemistry and various unusual physical properties [1–6]. TMDs can be typically represented as MX₂, where M stands for the transition metal and X is one of the chalcogenides (S, Se, Te). Structurally they could be stacked by X-M-X sandwiches, with strong covalent intralayer bonding, while the interlayer bonding is weak van der Waals interaction. Depending on the different composition and atoms arrangement, TMDs could be semiconducting, metallic, and/or even superconducting [7–10].

Recently, IrTe₂ and AuTe₂ have triggered a considerable interest in transition metal ditellurides due to the peculiar structural phase transitions and the emergence of superconductivity upon chemical doping or intercalation [11–17]. As regards IrTe₂, it undergoes a structural transition at ~ 270 K from the trigonal ($P\bar{3}m1$) to the monoclinic ($C2/m$) structure, accompanied by distinct anomalies in transport, magnetic, optical,

and thermodynamic properties [18–20]. Interestingly, this structural transition can be quickly suppressed in Ir_{1-x}(Pt/Pd)_xTe₂, (Pd/Cu)_xIrTe₂, or Ir_{1-x}Rh_xTe₂, and superconductivity appears at low temperatures [21,22]. The origin of this structural transition is widely discussed, including formation of a charge/orbital density wave or orbital Peierls state [12,13], kinetic energy [18], and Te 5p bonding instabilities [19], which is still under debate.

In TaTe₂, a structural transition at ~ 170 K is also observed, which has not been paid close attention to yet [23]. For TaTe₂, the room temperature structure is a monoclinically distorted CdI₂-type with the $C2/m$ space group, in which it forms double zigzag Ta chains along the b -axis direction [24–26]. The structural change at ~ 170 K upon cooling is reflected by further clustering of Ta atoms [23]. In the previous report, the structural distortion of TaTe₂ was investigated in M-substituted Ta_{1-x}M_xTe₂ with M = Ti, Zr, Hf, V, and Nb, indicating that the electronic effect plays a major role rather than the size of the substituting cation [27]. However, the origin of the structural transition of TaTe₂ has not been discussed, and its effect on the physical properties, especially the Hall

^(a) E-mail: wjlu@issp.ac.cn

^(b) E-mail: ypsun@issp.ac.cn

resistivity and thermoelectric property, has not yet been clarified.

Isovalent substitution is an effective method to clarify the origin of the structural transition in terms of tuning structural parameters, ionic size and/or electronegativity of elements [22,28]. In this study, a series of high-quality isovalent Nb-substituted distorted $1T$ - $\text{Ta}_{1-x}\text{Nb}_x\text{Te}_2$ ($0 \leq x \leq 1$) single crystals has been grown via the chemical-vapor-transport (CVT) method. Systematic X-ray diffraction (XRD), electrical resistivity (ρ), heat capacity (C_p), and especially, the Hall resistivity (R_H) and thermoelectric (S) measurements have been performed. The local chemical bonding instability is proposed to be responsible for the structural phase transition in the TaTe_2 system.

Experimental. – The single crystals were grown via the CVT method with iodine as a transport agent. Stoichiometric amounts of high-purity elements Ta, Nb, and Te were mixed and heated at 850°C for 4 days. Then the obtained $\text{Ta}_{1-x}\text{Nb}_x\text{Te}_2$ powder and iodine (density: 5 mg/cm^3) were sealed and heated for 10 days in a two-zone furnace, where the temperature of source and growth zones were fixed at 900°C and 800°C , respectively. The XRD pattern was obtained on a Philips X’pert PRO diffractometer with $\text{Cu } K_\alpha$ radiation ($\lambda = 1.5418\text{ \AA}$). The average stoichiometry was determined by examination of multiple points using X-ray energy dispersive spectroscopy (EDS) with a scanning electron microscopy (SEM). The EDS result indicates that the actual concentration x is close to the nominal one. The electrical resistivity (ρ), heat capacity (C_p), Hall resistivity (R_H), and thermoelectric (S) measurements were carried out in a Quantum Design Physical Property Measurement System (PPMS).

Results and discussion. – The single crystals of $\text{Ta}_{1-x}\text{Nb}_x\text{Te}_2$ ($0 \leq x \leq 1$) are black with metallic luster. TaTe_2 and NbTe_2 are typical TMDs with the monoclinically distorted CdI_2 -type structure with the $C2/m$ space group. Figure 1(a) shows the single crystal XRD patterns at room temperature, reflecting the preferred orientation. With increasing x , the diffraction peaks distinctly shift to the higher angle degrees, confirming the lattice contraction caused by smaller Nb substitution. Figure 1(b) exhibits the enlargement of the (-804) peak. Furthermore, several single crystals were crushed and used in the powder XRD experiment. As shown in fig. 1(c), the powder XRD patterns of $x = 0, 0.5$, and 1 are similar except for the slightly different relative peak intensity and slight shifts in positions, implying the series of $\text{Ta}_{1-x}\text{Nb}_x\text{Te}_2$ ($0 \leq x \leq 1$) crystallizes in the same structure. All the reflections could be indexed with the space group $C2/m$. The refined lattice parameters of $x = 0$ are $a = 14.781(9)\text{ \AA}$, $b = 3.638(2)\text{ \AA}$, $c = 9.341(5)\text{ \AA}$ and $\beta = 110.89(4)^\circ$. For $x = 0.5$, the lattice parameters are $a = 14.723(7)\text{ \AA}$, $b = 3.638(5)\text{ \AA}$, $c = 9.329(4)\text{ \AA}$ and $\beta = 110.45(3)^\circ$. For $x = 1$, the lattice parameters are $a = 14.682(7)\text{ \AA}$, $b = 3.638(1)\text{ \AA}$, $c = 9.319(4)\text{ \AA}$ and $\beta = 110.16(3)^\circ$. Undoubtedly, the values of a , c , and β

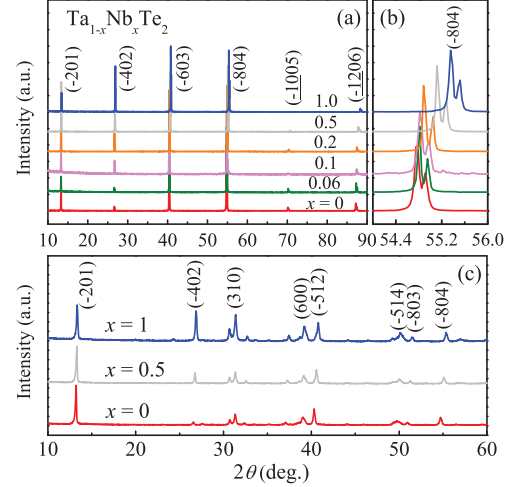


Fig. 1: (Color online) (a) Single-crystal XRD patterns of $\text{Ta}_{1-x}\text{Nb}_x\text{Te}_2$ ($0 \leq x \leq 1$). (b) The enlargement of the (-804) peak. (c) Powder XRD patterns for $x = 0, 0.5$, and 1 .

monotonously decrease with increasing x due to slightly smaller ion radius of Nb than that of Ta atom. The a -axis contraction δ_a is about 0.67% ($\delta_a = (a_{x=1} - a_{x=0})/a_{x=0}$), which is about three times larger than the c -axis variation $\delta_c \sim 0.23\%$. However, the value of the lattice parameter b is almost unchanged, implying the crystal structure is stable for all the Nb doping levels.

Figure 2(a) shows the room temperature structure of $\text{Ta}_{1-x}\text{Nb}_x\text{Te}_2$ ($0 \leq x \leq 1$), which is a monoclinically distorted CdI_2 -type structure with corrugated Te sheets [29]. Double zigzag Ta/Nb chains, also called ribbon-chain-type clustering, are formed along the b -axis, as shown in fig. 2(b). The atomic force microscopy (AFM) and scanning tunneling microscopy (STM) studies of TaTe_2 and NbTe_2 have made clear that the corrugated Te sheet is affected strongly by the modulation of the neighbor Ta/Nb layer [26]. It is worth noting that the double zigzag chains of the Ta/Nb atoms are considered to be intermediate between the $\sqrt{13} \times \sqrt{13}$ clusters of the d^1 configuration of $1T$ - TaS_2 and the zigzag chains of the d^2 configuration of $1T$ - MoTe_2 [26,30]. In the ionic picture, the Ta (Nb) atom has a $5d^36s^2$ ($4d^45s^1$) configuration, at the same time, the Te atom has a $5s^25p^4$ configuration, missing two electrons for a filled shell. Therefore, TaTe_2 and NbTe_2 will be nominally in a d^1 configuration. However, the recent calculations indicate that there is a stronger interaction between Ta/Nb and Te atoms and the Te $5p$ -derived valence bands overlap the Ta/Nb $5d$ bands significantly [31]. A local chemical-bonding consideration suggests the lattice distortion brings about a considerable electron transfer from the Te $5p$ valence bands to the Ta/Nb $5d$ bands and therefore the formal d electron count is $d^{4/3}$ other than the nominal d^1 [32]. This suggestion was also confirmed by the X-ray photoelectron spectroscopy (XPS) and the inner-shell-electron energy-loss spectroscopy (ISEELS) studies [26].

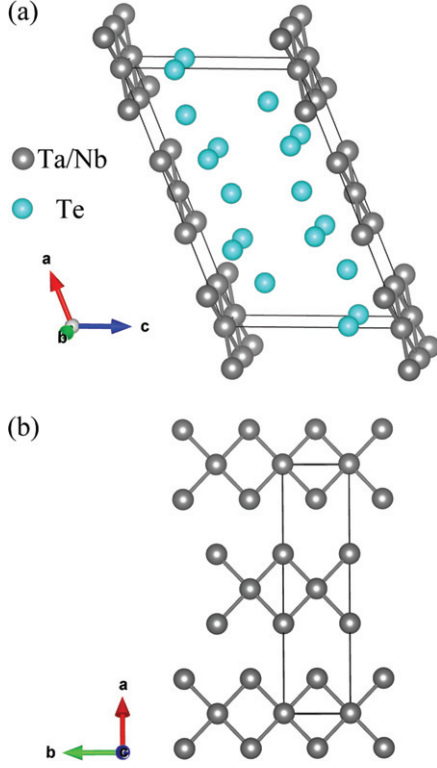


Fig. 2: (Color online) (a) Crystal structure of Ta_{1-x}Nb_xTe₂ ($0 \leq x \leq 1$) at room temperature. (b) The formation of double zigzag Ta/Nb chains.

Figure 3 shows the temperature dependence of the in-plane resistivity ratio (ρ/ρ_{2K}) of Ta_{1-x}Nb_xTe₂ ($0 \leq x \leq 1$) with the temperature range $2\text{ K} \leq T \leq 350\text{ K}$. The values of room temperature resistivity (ρ_{300K}) are about $143\text{ }\mu\Omega\text{ cm}$ and $54\text{ }\mu\Omega\text{ cm}$ for $x = 0$ and $x = 1$, respectively. The electrical transport behaviors are uniformly metallic type, for which the resistivity monotonically decreases with decreasing temperature. The superconductivity is absent in TaTe₂ [33], while NbTe₂ exhibits superconductivity at 0.5 K [34]. For the series of Ta_{1-x}Nb_xTe₂, no superconductivity above 2 K was obtained. However, it is interesting that a step-like anomaly is observed at $\sim 180\text{ K}$ for $x = 0$, of which the temperature is defined as the maximum of $d\rho/dT$, as shown in fig. 3. The resistivity shows slight decrease at the transition temperature upon cooling. It is in contrast to the experience from many of the other TMDs with the formation of charge density wave (CDW), which typically show an increase of resistivity due to the presence of gapping in the Fermi surface. With increasing x , the resistivity anomaly shifts to $T \sim 146\text{ K}$ for $x = 0.06$ and $T \sim 123\text{ K}$ for $x = 0.1$, and then disappears as $x \geq 0.2$, indicating the transition is gradually suppressed by Nb substitution. Additionally, the value of residual resistivity (ρ_{2K}) is $\sim 9.3\text{ }\mu\Omega\text{ cm}$ for $x = 0$, and it quickly increases to the maximum $\sim 55.9\text{ }\mu\Omega\text{ cm}$ for $x = 0.1$, and then decreases to $\sim 8.6\text{ }\mu\Omega\text{ cm}$ for $x = 1$, as shown in the left inset of fig. 3(b). The value of residual resistance

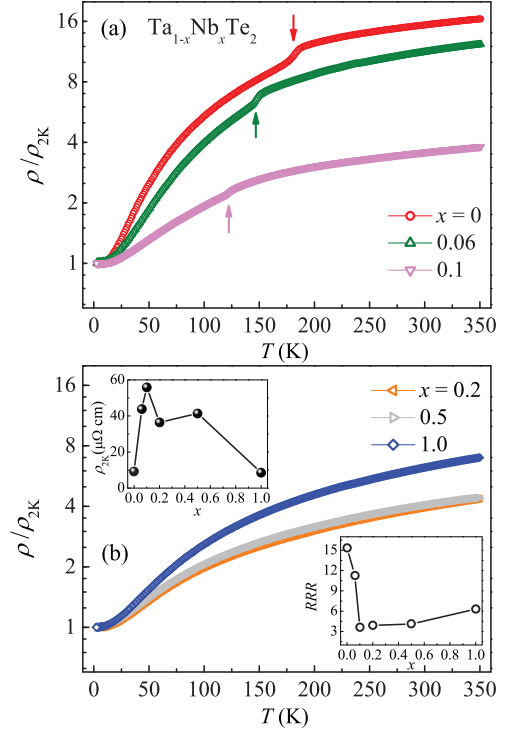


Fig. 3: (Color online) (a) The temperature dependence of in-plane resistivity ratio (ρ/ρ_{2K}) for $x = 0, 0.06$, and 0.1 . (b) The temperature dependence of ρ/ρ_{2K} for $x = 0.2, 0.5$, and 1 . Insets: the evolution of residual resistivity (ρ_{2K}) and residual resistance ratio ($RRR = \rho_{300K}/\rho_{2K}$).

ratio ($RRR = \rho_{300K}/\rho_{2K}$) also shows a minimum ~ 3.6 for $x = 0.1$, as shown in the right inset of fig. 3(b). The residual resistivity and RRR are indicators of disorder in the sample. That is to say, the sharp increase in the residual resistivity indicates that significant disorder is induced by Nb substitution and probably gives rise to the suppression of the phase transition.

In order to study the type of carriers and the anomalous transition in TaTe₂ ($x = 0$), the Hall coefficient (R_H) and thermoelectric power (TEP) are systematically measured. The magnetic field dependence of the Hall resistivity $\rho_{xy}(H)$ at various temperatures is shown in fig. 4. The Hall coefficient $R_H (= \rho_{xy}(H)/H)$ shows a positive value, indicating the hole-type carriers dominate the transport. The inset of fig. 4 shows the calculated density of carriers ($n = 1/|eR_H|$), which shows a slight upturn at $T \sim 180\text{ K}$, in accordance with the temperature of the resistivity anomaly. Furthermore, the TEP measurements of Ta_{1-x}Nb_xTe₂ ($0 \leq x \leq 1$) were performed within the temperature range from 320 K to 5 K , as shown in fig. 5. For TaTe₂ ($x = 0$), the $S(T)$ shows positive values in two temperature regions, namely, $T \geq 180\text{ K}$ and $T \leq 50\text{ K}$. The room temperature S_{300K} of TaTe₂ ($x = 0$) is about $5\text{ }\mu\text{V K}^{-1}$, and the $S(T)$ shows weak temperature dependence in the high-temperature region. However, the $S(T)$ sharply drops at around $T = 180\text{ K}$, coinciding with the temperature of the anomaly observed in resistivity

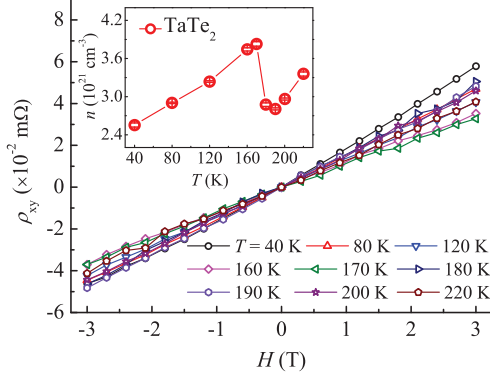


Fig. 4: (Color online) The magnetic field dependence of Hall resistivity $\rho_{xy}(H)$ at various temperatures for $x = 0$. Inset: the temperature dependence of carrier density $n = 1/|eR_H|$ based on the single-band model.

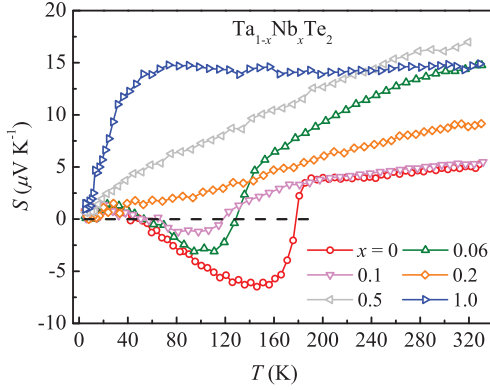


Fig. 5: (Color online) The temperature dependence of thermoelectric power $S(T)$ for $\text{Ta}_{1-x}\text{Nb}_x\text{Te}_2$ ($0 \leq x \leq 1$).

and Hall coefficient, and significantly, changes its sign at this temperature, implying a possible Fermi surface reconstruction [35–38]. A minimum about $-6.5 \mu\text{V K}^{-1}$ is observed at $T = 146 \text{ K}$ for TaTe_2 ($x = 0$). Additionally, the sign change of the $S(T)$ also implies multi-band transport [39]. Even though the Hall coefficient R_H is unchanged in this temperature range, the sign of $S(T)$ might change since they have a different dependence on carrier density n_e (n_h), mobility μ_e (μ_h), and S_e (S_h) in the two-band model [40]

$$R_H = \frac{n_h \mu_h^2 - n_e \mu_e^2}{e(n_h \mu_h + n_e \mu_e)^2}, \quad (1)$$

$$S = \frac{S_e n_e \mu_e + S_h n_h \mu_h}{n_e \mu_e + n_h \mu_h}. \quad (2)$$

With increasing x , the $S(T)$ anomaly is gradually suppressed and disappears as $x \geq 0.2$, implying the Nb-substitution suppresses the structural phase transition of TaTe_2 ($x = 0$) and the hence corresponding Fermi surface reconstruction.

Figure 6 exhibits the heat capacity (C_p) of $\text{Ta}_{1-x}\text{Nb}_x\text{Te}_2$ with $x = 0, 0.06$, and 0.1 . For $x = 0$, the

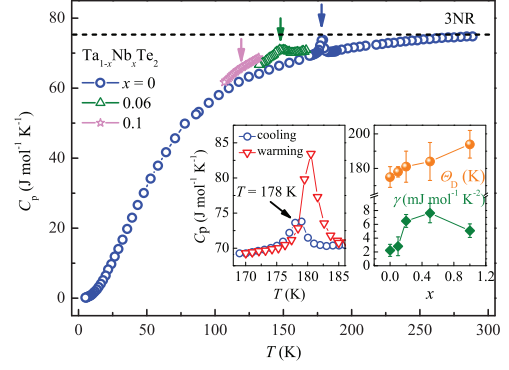


Fig. 6: (Color online) The temperature dependence of heat capacity C_p for $\text{Ta}_{1-x}\text{Nb}_x\text{Te}_2$ with $x = 0, 0.06$, and 0.1 . Insets: the enlargement of the specific-heat anomaly for $x = 0$ and the evolution of γ and Θ_D as a function of doping level.

specific-heat approaches the value of $3NR$ ($N = 3$ and $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) at high temperature, in accord with the Dulong-Petit law. The λ -shape peak is observed at $\sim 178 \text{ K}$ upon cooling for $x = 0$, which is gradually suppressed with increasing x , as shown in fig. 6. The left inset of fig. 6 exhibits the clear thermal hysteresis between the heating and cooling cycle for $x = 0$, showing the phase transition is first order in nature. Furthermore, we fitted the specific-heat curve between 5 K and 12 K by using the formula

$$\frac{C_p}{T} = \gamma + \beta T^2, \quad (3)$$

where γ is the Sommerfeld electronic specific-heat coefficient and β is the low-temperature limit of the lattice heat capacity. The obtained $\gamma \sim 2.2(9) \text{ mJ mol}^{-1} \text{ K}^{-2}$ of TaTe_2 ($x = 0$) and the derived Debye temperature $\Theta_D \sim 175 \text{ K}$ from $\beta \sim 1.09(1) \text{ mJ mol}^{-1} \text{ K}^{-4}$ using the equation

$$\Theta_D = \left(\frac{12\pi^4 N R}{5\beta} \right)^{\frac{1}{3}}, \quad (4)$$

where $N = 3$ is the number of atoms per formula unit and R is the molar gas constant, are comparable to the values of IrTe_2 [11,18]. According to the Sommerfeld theory of metals, γ can be written as a function of the density of states (DOS) at Fermi level as

$$\gamma = \frac{\pi^2 k_B^2}{3} N(E_F) (1 + \lambda), \quad (5)$$

where $N(E_F)$ is the DOS at the Fermi level and λ is the electron-phonon coupling constant. Owing to $\lambda \geq 0$, the obtained value of $N(E_F)$ is below $0.9(3) \text{ states eV}^{-1} \text{ f.u.}^{-1}$. When Nb is doped at Ta sites, the derived Debye temperature Θ_D monotonously increases with increasing x , however, the γ increases to $\sim 7.6(14) \text{ mJ mol}^{-1} \text{ K}^{-2}$ for $x = 0.5$ and then slightly decreases to $\sim 5.1(9) \text{ mJ mol}^{-1} \text{ K}^{-2}$ for $x = 1$, as shown in the right inset of fig. 6. Because the value of γ is proportional to the DOS near the Fermi level,

the Nb substitution likely increases the area of Fermi surface accompanying the suppression of structural transition.

In spite of no superconductivity above $T = 2\text{ K}$ in $\text{Ta}_{1-x}\text{Nb}_x\text{Te}_2$ ($0 \leq x \leq 1$), the suppression of structural phase transition is observed as $x \geq 0.2$. For TaTe_2 , owing to the diffuse character of Te $5p$ -orbital and to the weaker electronegative character of Te compared to S and Se atoms, it yields a direct overlap between the valence band (VB) and the conduction band (CB) around the Fermi level, as studied by the density functional theory (DFT) calculations [41,42]. The VB/CB overlap is strong enough to induce an electron transfer that mainly affects the local Ta-Te bond strength. As a consequence of the important Ta($5d$)-Te($5p$) orbital mixing, this electron transfer is associated with a decrease of the number of occupied Ta-Ta bonding states [41]. That is to say, the weakening of the local Ta-Te (Ta-Ta) bonds are likely responsible for the instability of the TaTe_2 structure. The low-temperature modification of TaTe_2 ($x = 0$) is also studied in details [23], leading to further clustering of the Ta atoms. As Nb doping at Ta sites, the local chemical bonds, namely, the Ta/Nb-Te and Ta/Nb-Ta/Nb bonds, are mainly affected and probably responsible for the final absence of structural phase transition for $\text{Ta}_{1-x}\text{Nb}_x\text{Te}_2$ ($x \geq 0.2$). This local bonding instability picture is consistent with the conclusions of ref. [16] and ref. [17] for the IrTe_2 system.

Conclusion. – In summary, we have successfully prepared a series of distorted $1T$ - $\text{Ta}_{1-x}\text{Nb}_x\text{Te}_2$ ($0 \leq x \leq 1$) single crystals and systematically investigated the effect of isovalent Nb substitution on the physical properties of the crystals by means of electrical resistivity (ρ), heat capacity (C_p), Hall resistivity (R_H), and thermoelectric power (S) measurements. The first-order transition at $\sim 178\text{ K}$ of TaTe_2 ($x = 0$) is gradually suppressed by Nb substitution and disappears as $x \geq 0.2$. For TaTe_2 , the $S(T)$ sharply drops and changes its sign at the transition temperature, implying multi-band behavior and a possible Fermi surface reconstruction. The isovalent Nb substitution is helpful to understand the origin of the structural phase transition in terms of tuning structural parameters, ionic size or electronegativity of the element, suggesting the local chemical-bonding instability may play an important role.

This work was supported by the National Key Basic Research under Contract No. 2011CBA00111, the National Nature Science Foundation of China under Contract Nos. 11404342 and 11274311, the Joint Funds of the National Natural Science Foundation of China and the Chinese Academy of Sciences' Large-scale Scientific Facility (Grant No. U1232139), Anhui Provincial Natural Science Foundation under Contract No. 1408085MA11, and the Director's Fund under Contract No. YZJJ201311 of Hefei Institutes of Physical Science, Chinese Academy of Sciences.

REFERENCES

- [1] JELLINEK F., *J. Less-Common Met.*, **4** (1962) 9.
- [2] WILSON J. A., DISALVO F. J. and MAHAJAN S., *Adv. Phys.*, **24** (1975) 117.
- [3] SIPOS B., KUSMARTSEVA A. F., AKRAP A., BERGER H., FORRÓ L. and TUTIŠ E., *Nat. Mater.*, **7** (2008) 960.
- [4] CHANG J., REGISTER L. F. and BANERJEE S. K., *J. Appl. Phys.*, **115** (2014) 084506.
- [5] LI Y., TONGAY S., YUE Q., KANG J., WU J. Q. and LI J. B., *J. Appl. Phys.*, **114** (2013) 174307.
- [6] MIREMADI B. K. and MORRISON S. R., *J. Appl. Phys.*, **67** (1990) 1515.
- [7] MARSEGLIA E. A., *Int. Rev. Phys. Chem.*, **3** (1983) 177.
- [8] WILSON J. A. and YOFFE A. D., *Adv. Phys.*, **18** (1969) 193.
- [9] GAMBLE F. R. and SILBERNAGEL B. G., *J. Chem. Phys.*, **63** (1975) 2544.
- [10] CLERC F., BATTAGLIA C., CERCELLIER H., MONNEY C., BERGER H., DESPONT L., GARNIER M. G. and AEBI P., *J. Phys.: Condens. Matter*, **19** (2007) 355002.
- [11] PYON S., KUDO K. and NOHARA M., *J. Phys. Soc. Jpn.*, **81** (2012) 053701.
- [12] YANG J. J., CHOI Y. J., OH Y. S., HOGAN A., HORIBE Y., KIM K., MIN B. I. and CHEONG S.-W., *Phys. Rev. Lett.*, **108** (2012) 116402.
- [13] OOTSUKI D., WAKISAKA Y., PYON S., KUDO K., NOHARA M., ARITA M., ANZAI H., NAMATAME H., TANIGUCHI M., SAINI N. L. and MIZOKAWA T., *Phys. Rev. B*, **86** (2012) 014519.
- [14] ZHOU S. Y., LI X. L., PAN B. Y., QIU X., PAN J., HONG X. C., ZHANG Z., FANG A. F., WANG N. L. and LI S. Y., *EPL*, **104** (2013) 27010.
- [15] KAMITANI M., BAHRAMY M. S., ARITA R., SEKI S., ARIMA T., TOKURA Y. and ISHIWATA S., *Phys. Rev. B*, **87** (2013) 180501R.
- [16] KUDO K., ISHII H., TAKASUGA M., IBA K., NAKANO S., KIM J., FUJIWARA A. and NOHARA M., *J. Phys. Soc. Jpn.*, **82** (2013) 063704.
- [17] KITAGAWA S., KOTEGAWA H., TOU H., ISHII H., KUDO K., NOHARA M. and HARIMA H., *J. Phys. Soc. Jpn.*, **82** (2013) 063704.
- [18] FANG A. F., XU G., DONG T., ZHENG P. and WANG N. L., *Sci. Rep.*, **3** (2013) 1153.
- [19] CAO H. B., CHAKOUMAKOS B. C., CHEN X., YAN J. Q., MCGUIRE M. A., YANG H., CUSTELCEAN R., ZHOU H. D., SINGH D. J. and MANDRUS D., *Phys. Rev. B*, **88** (2013) 115122.
- [20] MATSUMOTO N., TANIGUCHI K., ENDOH R., TAKANO H. and NAGATA S., *J. Low Temp. Phys.*, **117** (1999) 1129.
- [21] KUDO K., KOBAYASHI M., PYON S. and NOHARA M., *J. Phys. Soc. Jpn.*, **82** (2013) 085001.
- [22] LEI H. C., WANG K. F., ABEYKON M., BOZIN E., WARREN J. B. and PETROVIC C., arXiv:1307.7029 (2014).
- [23] SÖRGE T., NUSS J., WEDIG U., KREMER R. K. and JANSEN M., *Mater. Res. Bull.*, **41** (2006) 9.
- [24] KIM S. J., PARK S. J., OH H. J., JEON I. C. and SONG S., *Bull. Korean Chem. Soc.*, **15** (1994) 1098.
- [25] KIM S. J., PARK S. J., JEON I. C., KIM C., PYUN C. and YEE K. A., *J. Phys. Chem. Solids*, **58** (1997) 659.
- [26] OHNO Y., *J. Solid State Chem.*, **142** (1999) 63.

- [27] LEE S. and NAGASUNDARAM N., *Chem. Mater.*, **1** (1989) 597.
- [28] OH Y. S., YANG J. J., HORIBE Y. and CHEONG S. W., *Phys. Rev. Lett.*, **110** (2013) 127209.
- [29] BROWN B. E., *Acta Crystallogr.*, **20** (1966) 264.
- [30] ORION I., ROCHA J., JOBIC S., ABADIE V., BREC R., FERNANDEZ C. and AMOUREUX J. P., *J. Chem. Soc. Dalton Trans.*, **20** (1997) 3741.
- [31] CANADELL E., JOBIC S., BREC R., ROUXEL J. and WHANGBO M. H., *J. Solid State Chem.*, **99** (1992) 189.
- [32] WHANGBO M. H. and CANADELL E., *J. Am. Chem. Soc.*, **114** (1992) 9587.
- [33] KIDRON A., *Phys. Lett. A*, **24** (1967) 12.
- [34] NAGATA S., ABE T., EBISU S., ISHIHARA Y. and TSUTSUMI K., *J. Phys. Chem. Solids*, **54** (1993) 895.
- [35] LALIBERTÉ F., CHANG J., LEYRAUD N. D., HASSINGER E., DAOU R., RONDEAU M., RAMSHAW B. J., LIANG R., BONN D. A., HARDY W. N., PYON S., TAKAYAMA T., TAKAGI H., SHEIKIN I., MALONE L., PROUST C., BEHNIA K. and TAILLEFER L., *Nat. Commun.*, **2** (2011) 432.
- [36] ROURKE P. M. C., BANGURA A. F., PROUST C., LEV-ALLOIS J., LEYRAUD N. D., LEBOEUF D., TAILLEFER L., ADACHI S., SUTHERLAND M. L. and HUSSEY N. E., *Phys. Rev. B*, **82** (2010) 020514R.
- [37] PASCUT G. L., HAULE K., GUTMANN M. J., BARNETT S. A., BOMBARDI A., ARTYUKHIN S., BIROL T., VANDERBILT D., YANG J. J., CHEONG S.-W. and KIRYUKHIN V., *Phys. Rev. Lett.*, **112** (2014) 086402.
- [38] TORIYAMA T., KOBORI M., KONISHI T., OHTA Y., SUGIMOTO K., KIM J., FUJIWARA A., PYON S., KUDO K. and NOHARA M., *J. Phys. Soc. Jpn.*, **83** (2014) 033701.
- [39] LIU R. H., TAN D., SONG Y. A., LI Q. J., YAN Y. J., YING J. J., XIE Y. L., WANG X. F. and CHEN X. H., *Phys. Rev. B*, **80** (2009) 144516.
- [40] SU T. H., LUE C. S. and KUO Y. K., *J. Appl. Phys.*, **104** (2008) 093705.
- [41] DOUBLET M. L., REMY S. and LEMOIGNO F., *J. Chem. Phys.*, **113** (2000) 5879.
- [42] SHARMA S., NORDSTROM L. and JOHANSSON B., *Phys. Rev. B*, **66** (2002) 195101.