Single crystal growth of Ti doped VTe_2 and the elucidation of the electronic structure by ARPES

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Transition metal dichalcogenides, MX_2 show various kinds of physical properties such as charge density wave and superconductivity. In this research, we pay attention to VTe_2, which shows the structural phase transition at around 480 K from trigonal to monoclinic phase with zig-zag chains of transition metals. To clarify the origin of the structural phase transition, we have grown the single crystal of Ti doped VTe_2, measured the transport properties, and observed the electronic structure by angle resolved photoemission spectroscopy (ARPES). As a result, we have succeeded in synthesizing the large single crystal, which shows the structural phase transition below room temperature. From ARPES measurements, we have observed the hole-type Fermi surfaces near the Γ point and K point. We have also observed the formation of the gap at E_F in the band dispersion along the M point to the K point.

Introduction of the authors

Manabu Kamitani : M. K. specializes in the synthesis of novel materials and the measurements of the transport properties of them. His research interest is on the development of novel materials with peculiar physical properties based on the controlling of the structural phase transition.

Tatsuya Sonobe : T. S. specializes in the ARPES measurement. His research interest is on the electronic structure of the iron-based superconductors.

How we started our collaborative research

This collaborative research was suggested by M. K. after he heard the presentations of T. S.. To understand strictly the physical properties near the structural phase boundary, it is insufficient to measure only the basic physical properties like resistivity, magnetic susceptibility, and heat capacity, so it is necessary to observe the electronic structure of solids directly. M. K. expected that he would be able to understand his material deeply by ARPES measurement. T. S. gave his ready consent of his interest for understanding the novel materials except iron-based superconductors. Even though the research areas of M. K. and T. S. are overlapped, it is difficult to discuss and conduct research mainly by students in the usual collaborative research. However, it is important to experience for conducting research by students themselves , we have applied the collaborative research course of MERIT.

The background and motivation of our research

The research for transition metal dichalcogenids has been the important issue in the condesed matter physics for several decades [1]. The reason is that these materials show various kinds of physical properties such as charge density wave and superconductivity and some of the origins of these physical properties have not been resolved yet. Moreover, MX_2 has been paid attention as a convincing candidate materials for valleytronics. It is expected that the research for MX_2 will be more developed in the future in the aspects of application and basic physics, so understanding the basic physical properties of them must be the important subject. In this research, we have paid attention to VTe_2, which shows the nontrivial structural phase transition. Let us explain VTe_2 and related materials below.

First, we see the crystal structure of VTe_2. Figure 1(a) shows the crystal structure of VTe_2 at high temperature phase. The crystal structure of VTe_2 is called 1T structure. In this layered structure, transition metal ions are arranged as trigonal lattice and the chalcogen ions with trigonal lattice are octahedrally coordinated [9] Each layer is interacted by Van der Waals force, resulting in the quasi two dimensional crystal structure.

Next , we see the physical properties of VTe_2. VTe_2 shows the structural phase transition at around 480 K from trigonal structure to monoclinic structure [2]. In the low-temperature monoclinic phase, the transition metals form zig-zag structure as shown in the inset of Fig. 1(c). Let us take notice for two points. The first point is that other group 5 tellurides, $NbTe_2$ and $TaTe_2$, have the same monoclinic structure. In these materials, the trigonal structure has not been ascertained and it has not been able to see the electronic structure of high temperature trigonal phase. The second point is that the origin of the structural phase transition has not been resolved yet, although the typical Fermi surface nesting scenario has been suggested [4]. M. K. noticed that VTe_2 has a relatively low structural phase transition temperature and $TiTe_2$ has a simple trigonal structure down to the lowest temperature. Then he tried the precise control of

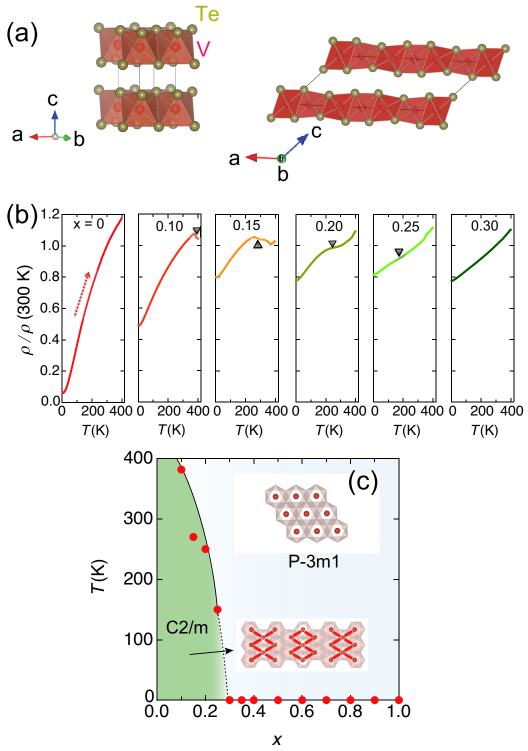

FIG. 1: (Color online) (a) The crystal structure of VTe_2. The left figure shows the trigonal structure, and the right one is the monoclinic structure. (b) Temperature dependence of resistivity of polycrystalline $V_{1-x}Ti_xTe_2$. (c) The electronic phase diagram for polycrystalline $V_{1-x}Ti_xTe_2$.

the structural phase transition of VTe_2 by Ti doping.

Finally, let us see the experimental results by M. K. for Ti doped VTe_2 before starting this collaborative research [3]. The temperature dependence of resistivity for polycrystalline $V_{1-x}Ti_xTe_2$ is shown in Fig. 1(b). Here, we show only the data for warming process. As increasing the Ti content, the anomaly of resistivity due to the structural phase transition gradually goes down to lower temperature. By more than 30 % Ti doping, no anomaly is not observed and the trigonal phase is stabilized down to the lowest temperature. These results are summarized as the electronic phase diagram shown in Fig. 1(c).

The purposes of this collaborative research are to synthesize the single crystal of Ti doped VTe_2 with showing the structural phase transition below room temperature and see the change of electronic structure by the structural phase transition by ARPES measurement. By the ARPES measurement, we have not been able to get the clear answer for the origin of the structural phase transition, but the energy gap formation near E_F by the structural phase transition has been observed.

Experimental details

We synthesized the single crystal of $V_{0.7}Ti_{0.3}Te_2$ by chemical vapor transport (CVT) method. We used $TeCl_4$ as a transport agent for CVT. The temperature dependence of resistivity was measured using PPMS (Quantum Design). Band structure calculation for trigonal VTe_2 was carried out by using WIEN2k [5]. We took the hypothetical trigonal structure estimated from the result of structure refinement for Ti doped VTe_2. For simplicity, we did not take into account the effect of spin-orbit coupling. ARPES measurement was performed at Ishizaka laboratory with He discharge lamp and R4000 photoelectron analyzer (VG-Scienta). We set up the excitation energy as 21.2 eV (HeIα) and the energy resolution as about 20 meV. The sample was cleaved in the vacuum state (3×10^{-10} Torr). We took the data at 300 K (trigonal phase) and 100 K (monoclinic phase) in the pressure as 1×10^{-10} Torr.

Results and discussion

Fig. 2(a) shows the picture of single crystal of $V_{0.7}Ti_{0.3}Te_2$ synthesized by CVT. We have succeeded in synthesizing large single crystal with several mm square. We can ascertain the good cleavage of the sample and the sample grows in-plane direction. Next, we show the XRD patterns of the single crystal in Fig. 2(b). The peaks corresponding to (0 0 l) of the trigonal phase are clearly seen, indicating the good sample quality. The temperature dependence of resistivity for single crystal is shown in Fig. 2(c). The upturn of the resistivity is observed due to the structural phase transition from about 290 K to 270 K in the temperature cooling process and the normal metallic behavior is ascertained with further decrease of temperature. We can see the thermal hysteresis of the resistivity due to the first order nature of the phase transition. The expanded figure of the temperature dependence of resistivity near the structural phase transition is shown in the inset of Fig. 2(c). From the results above, we can ascertain that the single crystal, which shows the structural phase transition below room temperature, has been obtained.

Here, let us discuss the composition of the single crystal of $V_{0.7}Ti_{0.3}Te_2$. The polycrystalline sample of x = 0.30 shows no structural phase transition down to the lowest temperature as shown in Fig. 1(b). So the structural phase transition cannot be observed if the relation between the composition and the structural phase transition temperature of the single crystal corresponds to the polycrystalline samples perfectly. We consider two causes for this fact. First, the electronic phase diagram for the single crystals is different from that of polycrystalline samples. Second, the composition of the single crystal deviates from the prepared composition, result-

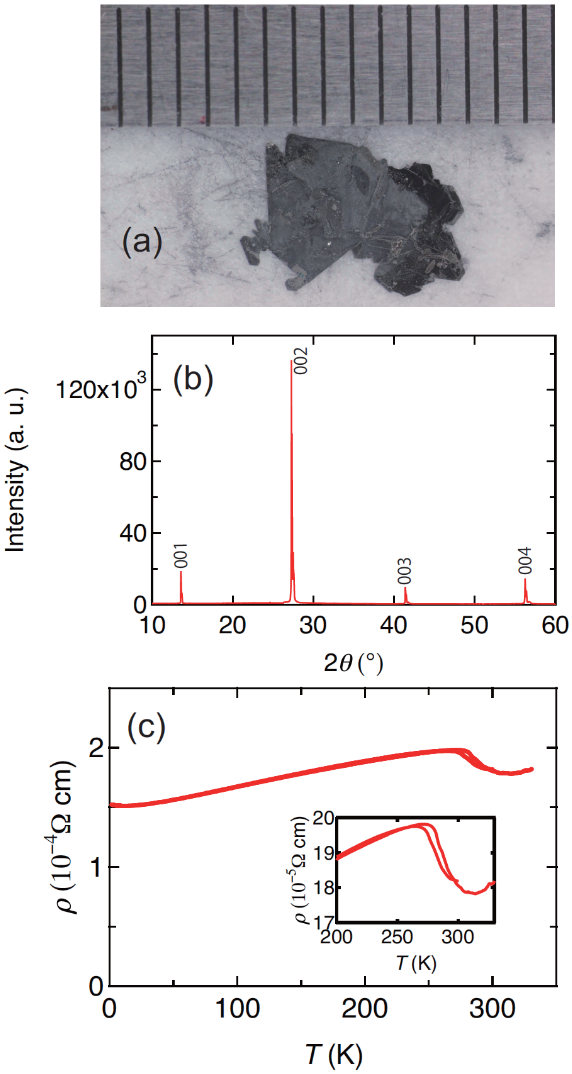

FIG. 2: (Color online) (a) The image of single crystal of $V_{0.7}Ti_{0.3}Te_2$. (b) The XRD patterns for single crystal of $V_{0.7}Ti_{0.3}Te_2$. (c) The temperature dependence of resistivity for single crystal of $V_{0.7}Ti_{0.3}Te_2$.

ing in synthesis of underdoped sample. In this collaborative research, we synthesized several compositions of single crystals, but we could not get the single crystals with high structural phase transition temperature above 400 K, so we have not succeeded in making the electronic phase diagram. The composition can be determined from SEM-EDX or comparison with c axis length to some extent [6], but we have not determined the strict composition for the measured sample.

Next, we see the results of ARPES measurements. Fig. 3(a) shows the image plot of Fermi surface for the trigonal phase, extracted from the integration of photoemission spectrum for each wave number at 300 K. The range of integration is ±10 meV from Fermi energy (E_F). The solid line and the dotted line indicate the 1st Brillouin zone projected to 2D and the Fermi surface obtained from ARPES measurements, respectively. The small Fermi surface at Γ point and the large Fermi surface at K point are observed. These Fermi surfaces are quite similar to those of $TaTe_2$ at $k_z = 0$ with hypothetical trigonal structure obtained from band structure calculation [7]. Figure 3(b) and (c) show the image plot of band dispersion along Γ point → K point and M point → K point, respectively. When we draw these image plots, we take second derivative for energy direction of each ARPES data to emphasize the peak positions. The photoemission intensity near E_F is much larger than that of the other energy region. Therefore, we show the small binding energy region (below 400 meV) and the high binding energy region in different color scales to see the entire band structure clearly. The different photoemission intensities between the high and low energy region come from the difference in the elements of determinant of photoelectron excitation process as pointed out in the previous work for $NbTe_2$ [4], because the orbital components of the band structure for each energy region. Corresponding to the Fermi surface plots in Fig. 3(a), the hole band near the Γ point and the hole band along the Γ point and the M point near the K point form the Fermi surfaces. Several hole bands are observed in the high binding energy region near the Γ point and the M point. These results coincide with the result of band structure calculation of VTe_2 ($k_z = 0$) as shown in Fig. 3(d). The good agreement between the experimental results and the band structure calculation indicate that the electron correlation in this system is not large and the variation of the electronic state by Ti doping is well described by rigid band picture.

Next, we see the results of ARPES measurements well below the structural phase transition temperature (100 K). In the low temperature monoclinic phase, the three folded lattice period is formed along the a-axis of the monoclinic structure as shown in the inset of Fig. 1(c). So, the observation of the folded band structure is expected because the BZ is folded by 1/3. It is also expected that the photoemission spectrum with overlapped electronic state of the domains, because three kinds of domains in the direction of broken rotational symmetry can be mixed in the spot of the excited photons. The BZ and the names of symmetric points in the figures and sentences are same as the trigonal phase for simplicity. Figure 4(a) shows the image plot of the second derivative of the spectrum along Γ point → K point at 100 K (monoclinic phase). The observed band dispersions are similar to those of the trigonal phase (see Fig. 3(b)), but some clear differences are seen. The first point is that the two bands at Γ point, which are degenerated at $E_B = 1.6$ eV in the trigonal phase, split in the monoclinic phase. The band structure calculation suggests that these bands are constructed from $p_x + p_y$ orbitals. The lifted degeneracy is strongly reflected in the in-plane component of the orbitals in the low-temperature mono-

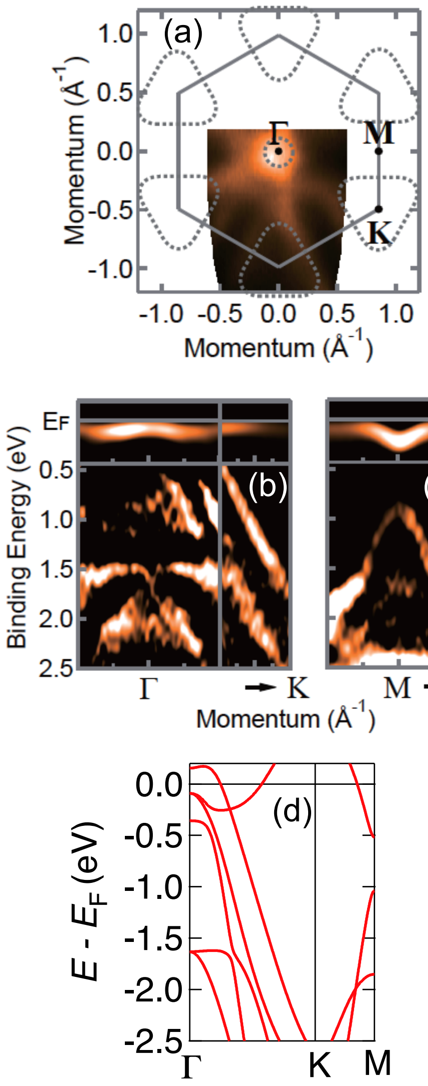

FIG. 3: (Color online) Results of the ARPES measurement for single crystal of $V_{0.7}Ti_{0.3}Te_2$ at 300 K and the band structure calculation. (a) Image plot of Fermi surface. (b) Image plot of band dispersions along Γ point → K point. (c) Image plot of the band dispersions along M point → K point. (d) Band structure of VTe_2 calculated from hypothetical trigonal phase.

clinic phase because of the broken rotational symmetry. The next point is that the energy gap is formed at the non-degenerate point of the hole band along K point. Even though such a change of the band structure is seen, the folded bands due to the lower symmetry of the crystal structure is not observed. In ARPES measurement, the band dispersions of the original crystal structure are easier to observe empirically than folded band dispersions coming from the superlattice formation. It is suggested that the effect of the formation of superstructure can be observed as the gap formation in the original band dispersions [8]. The gap in the non-degenerate points in the monoclinic phase can be interpreted as an gap formation at the band crossing points due to the fold of BZ. We also observe the change of electronic structure near E_{F}. We show the ARPES data along M point → K point near E_{F}. We can determine Fermi wave number (k_{F}) precisely (see the dotted lines of Fig. 4(b)), because there are few the band dispersions in this wave number region. Fig. 4 (c) shows the photoemission spectra at the k_{F} in the trigonal phase (300 K) and the monoclinic phase (100 K). In this plot, we exclude the effect of the difference of Fermi-Dirac distributions by dividing the Fermi-Dirac distribution function by the Gaussian folded function with half-width of the measurement resolution. Spectrum at 300 K has a peak at E_{F}. On the other hand, spectrum at 100 K does not have a peak and the intensity of the spectrum decreases from about $E_{\mathrm{B}} = 100$ meV. Energy of this gap agrees well with the result of ARPES experiment for $NbTe_2$, which has the same crystal structure as VTe_2 [4]. However, the ARPES measurements at temperatures above and below the structural phase transition can be carried out only in the single crystal of Ti doped VTe_2. From the ARPES measurements of this collaborative research, we clarify that the gap formation described above originates from the structural phase transition. From the band structure calculation for $NbTe_2$, the nesting of the Fermi surfaces is good between the large Fermi surfaces at the BZ corner with $q = a^*/3$ [4]. So the charge density wave scenario is suggested for the origin of the structural phase transition. The gap formation in the band dispersion along M point → K point observed in this collaborative research can support the suggestion of the previous work.

Summary of this collaborative research

We summarize the results of this collaborative research below. From the single crystal growth and resistivity measurement,

- We have succeeded in the growth of Ti doped VTe_2 single crystal by CVT with $TeCl_4$, which shows the structural phase transition below room temperature.

From the results of ARPES measurements for trigonal and monoclinic phase,

- The good agreement between the experimental results and band structure calculation indicate that the electron correlation in this system is not large and the variation of the electronic state by Ti doping is well described by rigid band picture.

- The gap formation in the band dispersion at E_{F} along M point → K point by structural phase transition is observed for the first time.

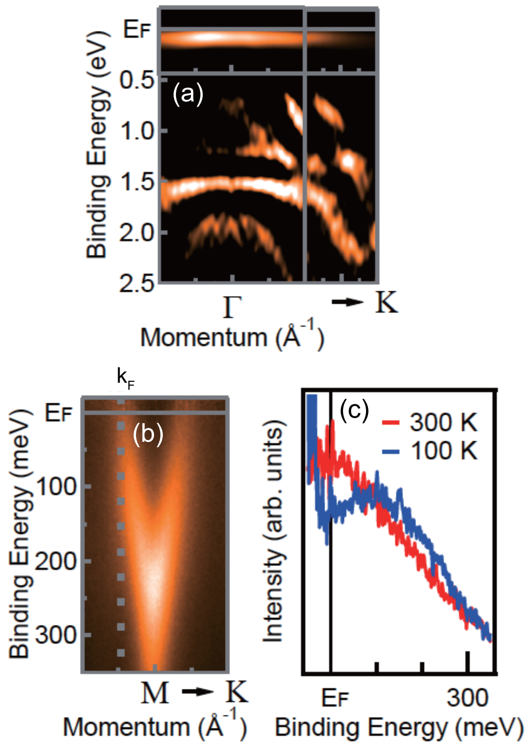

FIG. 4: (Color online) Results of ARPES measurement for single crystal of $V_{0.7}Ti_{0.3}Te_2$ at 100 K. (a) The image plot of the band dispersions along Γ point → K point. (b) Angle resolved photoemission spectrum near E_F along M point → K point. (c) Photoemission spectra estimated from (b) at Fermi wave number at 300 K and 100 K.

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[9] MX_2 can have various structures other than 1T structure, for example, 2H and 3R type with quasi-two dimensional structure and pyrite type. See the citing article 1 for detail.