Electronic structure of the BaV$_{1-x}$Ti$_x$S$_3$ system as studied by photoelectron spectroscopy

R. Itti, T. Wada, K. Matsuura, T. Itoh, K. Ikeda, H. Yamauchi,
N. Koshizuka, and S. Tanaka
Superconductivity Research Laboratory, International Superconductivity Technology Center,
1-10-13 Shinonome, Koto-ku, Tokyo 135, Japan
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X-ray and ultraviolet photoelectron-spectroscopic (XPS and UPS) studies to investigate the core levels and valence-band spectra of BaV$_{1-x}$Ti$_x$S$_3$, with $x = 0$ and 0.2, is reported. The XPS results indicate that the valence of V as well as Ti is not 4 as would be expected nominally, but between 3 and 4. Essentially no difference of the core-level binding energies was observed between the two samples. The valence-band spectra exhibit three peak features at about 1, 2.5, and 4 eV. From the enhancement of the peak at 1 eV by the He II photon, it is concluded that the V $3d$ orbitals are strongly incorporated in this peak that is close to the Fermi level. It is shown that the bond-valence-sum method can be useful as a quantitative tool for discussion of XPS results. The possibility of using the bond-valence-sum calculation for discussions on the transport properties of the system is also shown.

I. INTRODUCTION

BaVS$_3$ is a system showing some characteristics similar to those of the parent materials of high-T_c cuprate superconductors. It exhibits a magnetic transition at low temperature and a metal-to-nonmetal transition upon substitution. It is one of the systems interesting to those who are looking for the possibility of high-T_c superconducting in a noncuprate system.

The crystal structure of BaVS$_3$ at room temperature is hexagonal with space group $P6_3/mmc(D_{6h}^4)$. Each V atom is surrounded by six sulfur atoms forming an octahedron. These octahedra share faces and form continuous chains of V cations parallel to the c axis. The chains are separated by large barium ions. V atoms on the same chain are separated by 2.805 Å, while the distance between chains of V is 6.724 Å.[1] The existence of linear chains of V atoms is characteristic of this system. Since the valence of V in BaVS$_3$ is formally $4+$ with an electronic configuration $3d^1$, it can be considered as a good physical approximation of a one-dimensional magnetic system. By substitution of Ti^{4+} ($3d^0$) for V^{4+} ($3d^1$), it is possible to vary the number of d electrons in the chains. Electrical and magnetic changes associated with this should be of great interest.

The study of BaVS$_3$ and BaV$_{1-x}$Ti$_x$S$_3$ was stimulated firstly by the report of BaVS$_3$ of Gardner et al.[1] Although a number of structural, electrical, and magnetic studies have been carried out and much has been known about this system,[1-10] full understanding of the electronic structure has not yet been achieved. The relation of the existence of the V chains and the structural change with temperature to the transport and magnetic properties has been the main interest of the system. It is reported that the BaVS$_3$ system exhibits a structural phase transition from hexagonal to orthorhombic around 240 K.[1] Transport studies reveal that it is weakly metallic at temperatures above 150 K and weakly semiconducting below

this temperature.[1-4] At about 80 K a second phase transition takes place in the electric conductivity, magnetic susceptibility, and specific heat.[2-4] The existence of a third phase transition at about 31 K has also been pointed out.[7] Ghedira et al. have studied the crystal structure of this system at room and low temperature down to 5 K.[10] Based on this and the existing experimental results they have made an attempt to interpret the physical properties of the system. Recently, further investigation on the electrical and magnetic properties of the BaV$_{1-x}$Ti$_x$S$_3$ system for $0 \le x \le 0.2$ has been performed.[11] It was found that, for x in this range, the sign of the Seebeck coefficient was negative above about 70 K and changed to positive below this temperature. Upon substitution, the resistivity increased relative to that of BaVS$_3$ at the same temperature and showed a semiconductive characteristic temperature dependence. For the susceptibility, the peak at 70 K observed for BaVS$_3$ disappeared in the substituted samples. Further, the magnitude of the dc magnetic susceptibility decreased upon substitution.

In regard to the electronic structure, although a band model was proposed to account for the physical properties observed,[4] to our knowledge, no experimental or theoretical electronic study of this system exists. In this communication, the electronic structure of this system at room temperature investigated by XPS and UPS measurements is reported and discussed in connection with the physical properties.

II. EXPERIMENTAL

The samples used in this study were prepared by the following procedure. Powders of BaCO$_3$, V$_2$O$_5$, and TiO$_2$ were mixed in ethanol with the cation ratio of [Ba]:[V$_{1-x}$Ti$_x$] = 1:1. Next, the mixed powder was calcined at 600 °C for 5 h in H$_2$S-Ar mixture gas flow, slowly cooled down to room temperature and then ground. This

calcination process was repeated three times before the powder was pressed into pellets and calcined again under the same conditions. Finally, the pellets were heated in evacuated quartz ampoules at 800 °C for 20 h to obtain black ceramic BaV$_{1-x}$Ti$_x$S$_3$ samples. Sample characterizations were described in detail elsewhere.[11]

High-quality polycrystalline BaV$_{1-x}$Ti$_x$S$_3$ samples with $x = 0$ and 0.2 obtained by this method were used in this study. Measurements were made on an ultra high-vacuum (UHV) system equipped with an Al x-ray source ($h\nu = 1486.6$ eV) for x-ray photoelectron spectroscopy (XPS) and a noble-gas discharge lamp for ultraviolet photoelectron spectroscopy (UPS). The energy distribution of the photoelectrons was determined by an electron-energy analyzer, the resolution of which was set at 0.8 and 0.15 eV for XPS and UPS measurements, respectively. Core-level binding energies were referenced to the adventitious C 1s peak at 285.0 eV. For the UPS measurement, the Fermi energy was determined directly from the zero binding energy of the analyzer because no charge-up was observed and the accuracy was better than 0.2 eV. The typical pressure during measurements was about 2×10^{-10} Torr. The sample surface was scraped *in situ* by a diamond file to expose a fresh surface prior to each measurement. The surface cleanliness was confirmed by the absence of the adventitious C 1s peak. After scraping, no appreciable changes in the spectra were observed over the period of measurements which was typically 30 min. In this study, all of the spectra were taken at ambient temperature.

III. RESULTS AND DISCUSSION

A. Core-level spectra

Figures 1(a) and 1(b), respectively, show the V 2p and V 3p core-level XPS spectra from BaV$_{1-x}$Ti$_x$S$_3$ with $x = 0$ (solid line) and $x = 0.2$ (dotted line) samples. The binding energies (BE's) of the V core levels in both samples are almost identical, indicating that substitution of Ti for V by this amount (20%) does not significantly affect the BE's of V in the system. In various chemical environments, the BE of V 2$p_{3/2}$ can range between 511 and 517 eV.[12] The observed BE of V 2$p_{3/2}$ of 514.5 eV in this system is in between those for VN and VO$_2$ in which the valence of V is nominally 3 and 4, respectively. Thus, we may tentatively conclude that the valence of V in this system is likely to be in between 3 and 4, rather than the nominal valence of 4.

In Fig. 1(b), a peak indicative of the Ti 3p core-level can be observed at about 35 eV for the $x = 0.2$ sample. This is evident from its absence in the $x = 0$ spectrum as well as the good agreement with the reported binding energy.[12]

Figures 2(a) and 2(b), respectively, show the S 2s and S 2p core-level spectra from both samples. Also in this case, no significant changes in BE's for these core levels were observed between the $x = 0$ and $x = 0.2$ samples. A slight narrowing of the peak widths of S 2s and S 2p core levels in the $x = 0.2$ sample can be pointed out. The reason for this is not clear; this may be due to the sample
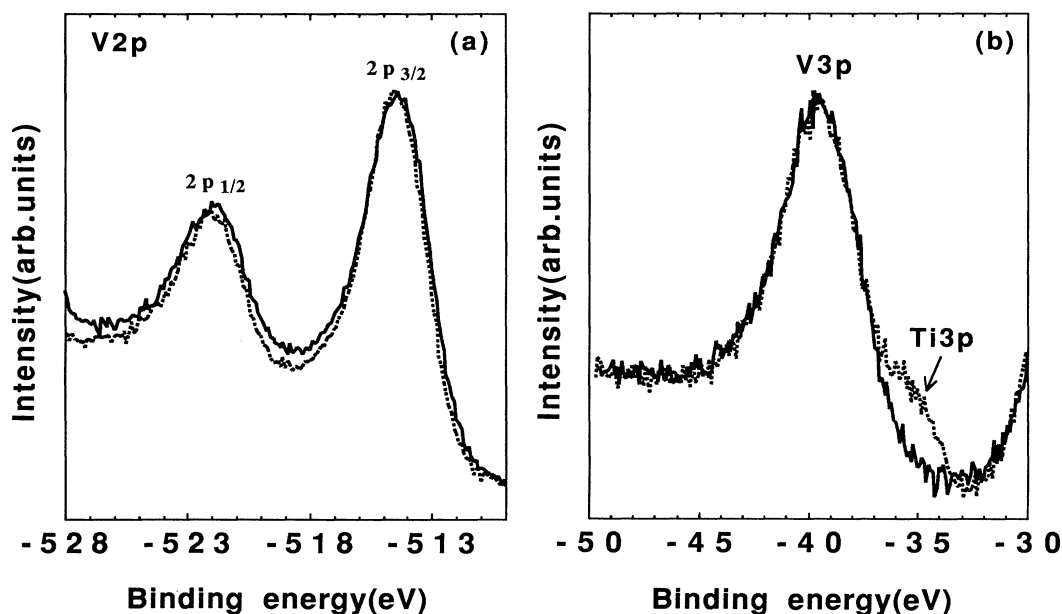

FIG. 1. V 2p (a) and V 3p (b) core-level XPS spectra from BaV$_{1-x}$Ti$_x$S$_3$ with $x = 0$ (solid line) and $x = 0.2$ (dotted line) samples.
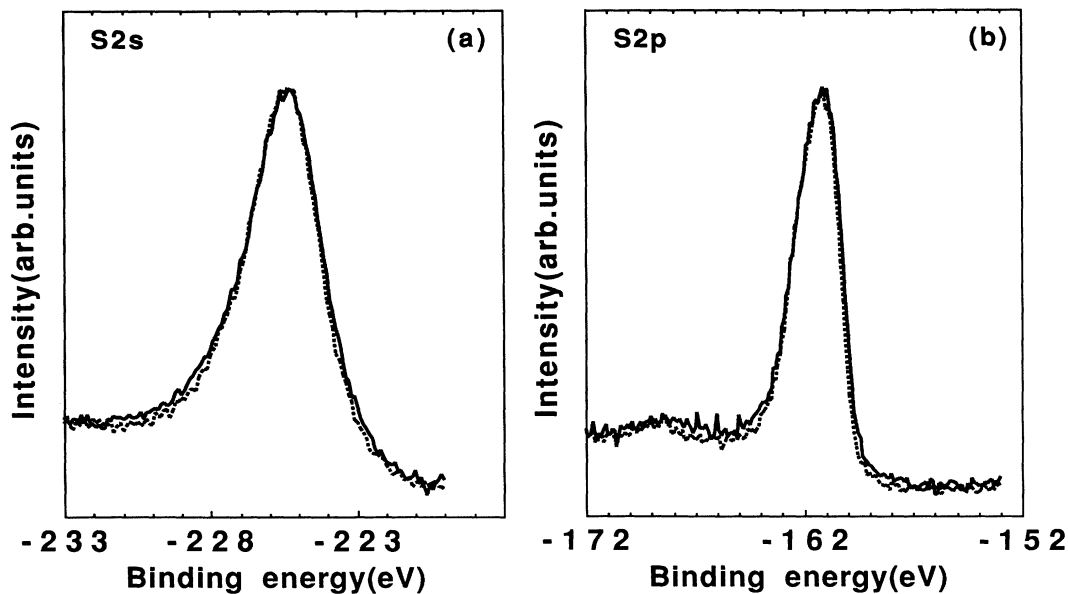
R. ITTI *et al.*

FIG. 2. S 2*s* (a) S 2*p* (b) core-level XPS spectra from $BaV_{1-x}Ti_xS_3$ with $x=0$ (solid line) and $x=0.2$ (dotted line) samples.

quality or may be intrinsic. The BE's of S 2*p* core level in both samples are 161 eV. In various chemical environments, the BE of the S 2*p* core level varies between 160–169 eV.[12] The fact that the observed values are nearly identical to those of S 2*p* in PbS and FeS, indicates that S ions in $BaV_{1-x}Ti_xS_3$ are divalent with similar chemical environments as in these compounds. This is not surprising considering the crystallographic similarities of S in $BaV_{1-x}Ti_xS_3$ and in PbS or FeS.[13]
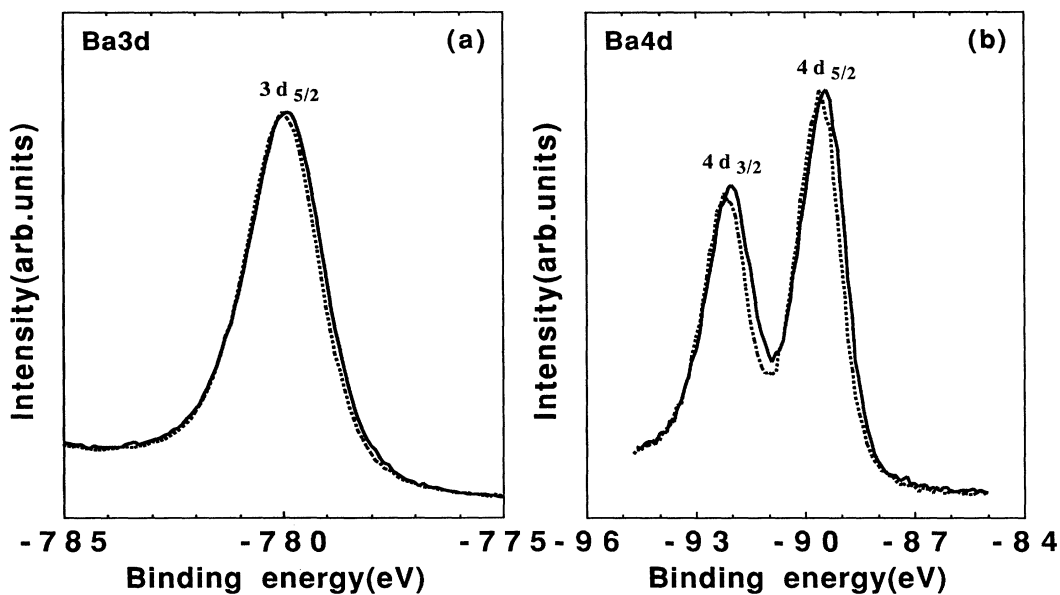
The Ba 3*d* and Ba 4*d* core-level XPS spectra from both

FIG. 3. Ba 3*d* (a) and Ba 4*d* (b) core-level XPS spectra from $BaV_{1-x}Ti_xS_3$ with $x=0$ (solid line) and $x=0.2$ (dotted line) samples.

samples are shown in Figs. 3(a) and 3(b), respectively. The observed BE of Ba $3d_{5/2}$ in $BaV_{1-x}Ti_xS_3$ is 779.9 eV for $x = 0$ and is 780.0 eV for $x = 0.2$. These values agree well with those reported for compounds with Ba ions.[12] The results indicate that the BE's of the Ba core levels in $BaV_{0.8}Ti_{0.2}S_3$ are slightly higher than those in $BaVS_3$. Together with the results of other core levels, it seems that substitution of Ti for V mainly affects the chemical environment of Ba ions rather than that of V or S ions. This is somewhat surprising since structurally Ba ion is farther away from the V site, where substitution occurs, than the V ion itself or than the S ions surrounding the V site. The reason for this is not clear. We will discuss this again later together with an insight from another point of view.

Figure 4 shows the Ti $2p$ core-level spectrum from the $BaV_{0.8}Ti_{0.2}S_3$ sample. The BE of the Ti $2p_{3/2}$ core level can vary in the range of 454–462 eV in various chemical environments.[12] The observed value of about 456.2 eV for this sample is in between those for TiS (454.4 eV) and TiO_2 ($\sim$458.5 eV), indicating that the valence of Ti in this compound is possibly in between 3 and 4. Although the same conclusion was made for V as described above, since it is unable to determine the valences of V and Ti from these XPS results quantitatively, to discuss the change of charge carriers upon substitution resulting in a metal-to-nonmetal transition in this system is not possible.

Figure 5 shows the XPS spectra in the valence-band and shallow core-level regions from both samples. Besides a broad valence band centered at about 4 eV binding energy, Ba $5p_{3/2}$ and Ba $5p_{1/2}$ core levels were ob-
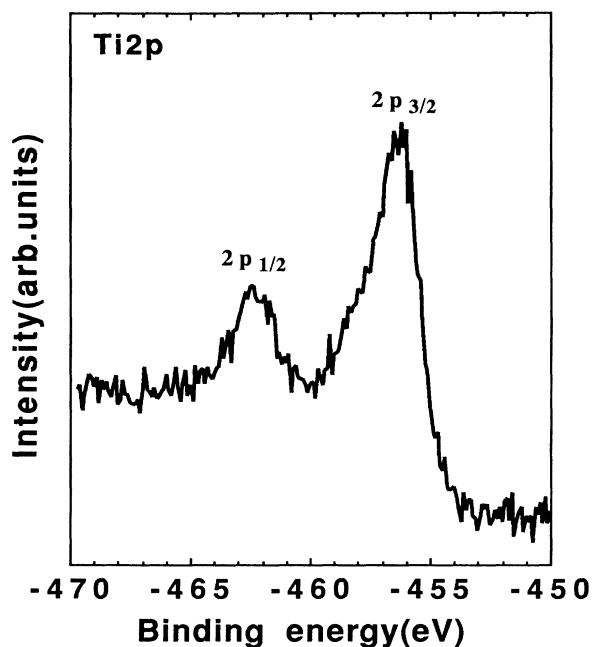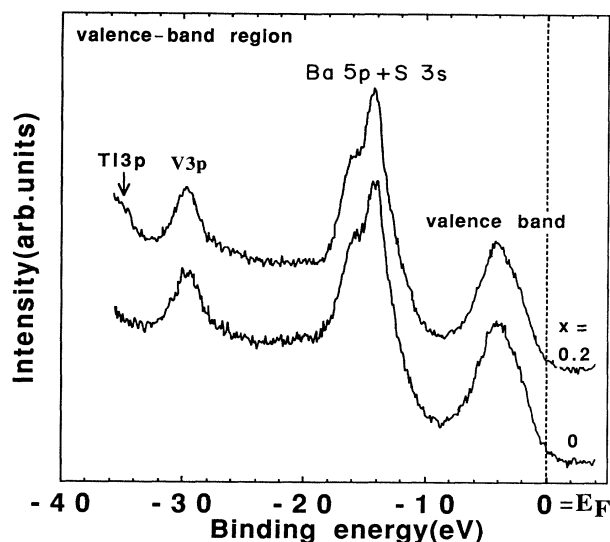

FIG. 5. XPS spectra in the valence-band and shallow core-level regions from $BaV_{1-x}Ti_xS_3$ samples with $x = 0$ and 0.2.

served at about 14 and 16 eV, respectively. For the Ti-substituted sample, as already mentioned in Fig. 1(b), the Ti $3p$ core level appears at about 35 eV. Next, we consider the peak at the 30-eV binding energy. It is well known that when a system has unpaired electrons in the valence levels, multiplet splitting (or exchange splitting) of core-level peaks can occur.[14] Since there is an unpaired V $3d^1$ electron in this compound, there is a possibility that the above-described multiple splitting would occur. In this conjecture we assign this peak at 30 eV as one of the split V $3p$ core levels with another at 40 eV as already assigned above [Fig. 1(b)]. This is supported by the fact that there is no possibility to assign this peak to other core levels, considering its peak shape, intensity, and binding energy. The energy separation of these two split peaks of about 10 eV is also reasonable with those values reported in literatures.[14]

B. Valence-band spectra

Figure 6 shows the UPS spectra in the valence-band region from both samples (solid line for the $x = 0$ and dotted line for the $x = 0.2$ samples). The upper two spectra, plotted on the same vertical scale, were recorded by the He I ($h\nu = 21.2$ eV) photon, while the bottom spectrum, shifted vertically, by the He II ($h\nu = 40.8$ eV) photon. Peak features at about 1, 2.5, and 4 eV can be observed in all spectra. Upon Ti substitution, the BE's of these peaks do not appear to shift. However, the relative intensity of the peak at about 2.5 eV for the $x = 0.2$ sample increased compared to that of the $x = 0$ sample. The relative decrease of the spectrum intensity at the high-binding-energy side for the $x = 0.2$ sample compared with that of the $x = 0$ sample can also be pointed out. Whether these relative changes in intensity are intrinsic or not, however,
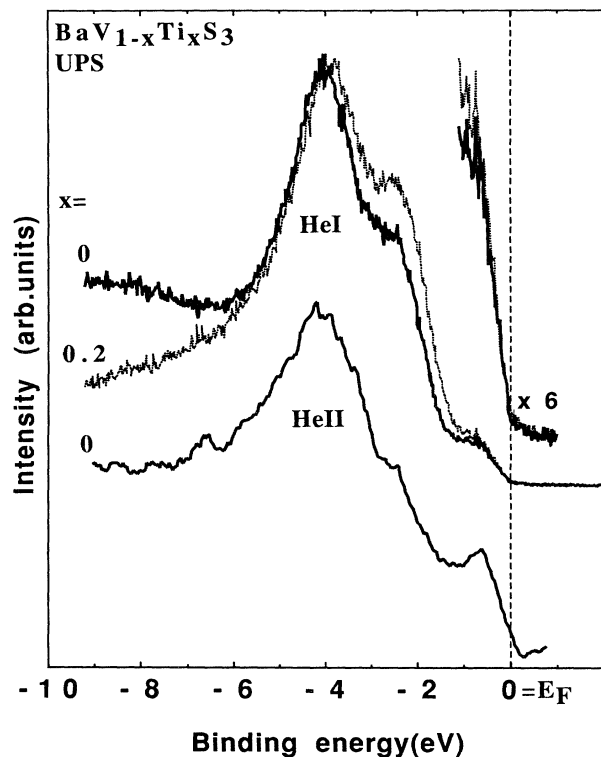

FIG. 4. Ti $2p$ core-level spectrum from the $BaV_{0.8}Ti_{0.2}S_3$ sample.

FIG. 6. Valence-band UPS spectra from $BaV_{1-x}Ti_xS_3$ samples with $x=0$ (solid line) and 0.2 (dotted line). The upper two curves were the He I ($h\nu=21.2$ eV) photon excited spectra, while the bottom one was the He II ($h\nu=40.8$ eV) photon excited (smoothed) spectrum of the $x=0$ sample. The enhancement of the He I photon–excited spectra in the Fermi level region is also shown.

is not clear from this study. Also in Fig. 6, the enhancement of the He I excited spectra in the Fermi level (E_F, BE of 0 eV) region is shown. The intensity of the spectra for both samples at the E_F is very small. This is consistent with the poor electrical conductivity of both samples. Although it is not clear from Fig. 6, there is evidence statistically concluded from a number of spectra for both samples indicating that the intensity at the E_F for $BaVS_3$ is somewhat larger than that of $BaV_{0.8}Ti_{0.2}S_3$. This is what is to be expected considering that in the room-temperature range this system is metallic with poor conductivity for $x=0$ and semiconducting for $x=0.2$ composition.[11] From the He II ($h\nu=40.8$ eV) photon excited UPS spectra, as also shown in Fig. 6 for the case of the $x=0$ sample, it is found that among the three peaks described above, the peak at about 1 eV is relatively enhanced. Since the He II photon energy is about at the resonant threshold for V $3p$-$3d$ excitation, the results indicate that the V $3d$ orbitals are strongly incorporated in this close to the E_F peak. This is in good agreement with the results of a band calculation recently performed on this system[15] and suggests that the $3d$ electrons in the V chains are responsible for the electrical and magnetic properties of this system.

C. Bond-valence-sum calculation and discussion

It is reported recently that the so-called bond-valence-sum (BVS) method,[16] where the valence of an atom can be quantitatively calculated from its interatomic distances with surrounding atoms, is useful for discussion of the change in the XPS core-level BE's in the system where the interatomic distances are varied either by substitution or temperature change.[17] We have calculated the valence of each atom in this system by this method based on the structural data reported by Ghedira *et al.*[10] to see if it is possible to make some quantitative discussion in relation with the XPS results. The calculated results are shown in Table I.

First, we discuss the $x=0$ sample. The BVS of V is 3.41. This supports our qualitative conclusion for the valence of V from the XPS results as described above (Fig. 1). The BVS of Ba and S are 2.21 and -1.87, respectively. These are different from their formal valences of $2+$ for Ba and $2-$ for S. Since deviation from formal valences of BVS is usually observed in a crystallographically constrained system,[18] it seems that this is the case for $BaVS_3$. Usually, in such a system, a finite electrical conductivity can be expected. The BVS results suggest that electrons are transferred from the Ba and S sites to the V sites, resulting in an effective valence of less than $4+$ for V and larger that $2+$ and $2-$ for Ba and S, respectively. The fact that the $BaVS_3$ system is metallic with negative Hall and Seebeck coefficients above 70 K (Ref. 11) suggests that the electrons on the V sites should play an important role in the transport properties of the $BaVS_3$ system. The short distance between the V-V atoms in the chain (2.805 Å) should also be a decisive factor.[19] Since, the sign of the Hall and Seebeck coefficients become positive at temperatures below 70 K (Ref. 11), it should be of great interest to investigate the structural changes and the associated changes of BVS at this low temperature range.

It was reported that the lattice parameters of this system change upon substitution.[4] Based on this we have estimated the interatomic distances and calculated the BVS for the $x=0.2$ sample as are also shown in Table I. Since the interatomic distances in reality may differ in a complicated manner from the estimated values, the results for the $x=0.2$ sample should be taken into account carefully and we will use this just for rough comparison with those of the $x=0$ sample. The results show that for 20% substitution, the BVS of V decreases but in a small amount. This explains why the BE's of the V core levels are almost identical between the two samples (Fig. 1). For Ti, the BVS is 3.60. This is in good agreement with the value qualitatively estimated from the XPS results for the Ti core level (Fig. 4). The average BVS on the V or Ti site for the $BaV_{0.8}Ti_{0.2}S_3$ composition is thus equal to 3.38. Comparison of this with the value of 3.41 for the $x=0$ sample shows that only a small change in the (average) BVS on a V or Ti site occurs, and we may conclude that there is no significant change in the number of electron carriers in the V chains upon 20% Ti substitution. Since the electrical conductivity of the system becomes poorer upon substitution,[11] we are led to conclude that the

TABLE I. Interatomic distances, r_{ij}, and bond valence sum (BVS) calculation for BaV$_{1-x}$Ti$_x$S$_3$.

Cation site		r_0[a]	BaVS$_3$ r_{ij}(Å)[b]	BVS[c]	BaV$_{0.8}$Ti$_{0.2}$S$_3$ r_{ij}(Å)[d]	BVS
V-S		2.176	2.3853×6	<u>3.408</u>	2.3948×6	<u>3.321</u>
Ti-S		2.206			2.3948×6	<u>3.602</u>
Ba sites	Ba-S	2.769	3.364×6	1.202	3.376×6	1.163
	Ba-S	2.769	3.428×6	1.011	3.442×6	0.973
				<u>2.213</u>		<u>2.136</u>
S sites	S-Ba	2.769	3.364×2	−0.401	3.376×2	−0.388
	S-Ba	2.769	3.428×2	−0.337	3.442×2	−0.324
	S-V	2.176	2.3853×2	−1.136	2.3948×2	−1.107
				<u>−1.874</u>		<u>−1.819</u>

[a]r_0's were taken from or calculated according to the method suggested by Brown and Altermatt (Ref. 16).

[b]Interatomic distances from data of Ghedira et al. (Ref. 10).

[c]BVS for an i site is calculated by $\sum_j \exp[(r_0 - r_{ij})/0.37]$ where j's are the surrounding sites (Ref. 16).

[d]Interatomic distances estimated based on data of Ghedira et al. (Ref. 10) and Massenet et al. (Ref. 4).

metal-to-semiconductor transition associated should be caused by the localization of electrons due to disorders (Anderson localization) rather than the change in carrier density in the chains. The randomness on the chains due to Ti($3d^0$) substitution for V($3d^1$) should play a great role in the metal-to-nonmetal transition. This conclusion is consistent with the physical properties reported recently by Matsuura et al.[11]

The BVS of Ba and S for the $x = 0.2$ sample show a slight decrease compared with those for the $x = 0$ sample. The changes are quite small that there should be no significant change in the BE's of these core levels between the two samples. This explains why the observed S core levels do not change between the two samples (Fig. 2). However, the slight shift to higher BE's for the Ba core levels in the $x = 0.2$ sample compare with those of the $x = 0$ sample (Fig. 3) cannot be explained by this BVS estimation for Ba because BE should shift to lower value in a chemical environment with lower valence. It is plausible that the observed shift of the Ba core levels is not intrinsic but due to the quality of the samples or surfaces investigated. However, since the shift is very small, we believe that there should be no effect on the discussion and conclusion made in this report.

The above discussion shows that the bond-valence-sum method in which only structural data are needed seems to be useful to some extent for the discussion of the XPS results in that, not only the obtained valences agree well with those estimated from the XPS core levels, but also we can make some discussion in relation to the electrical and magnetic properties of the system. Since precise

structural data as a function of x for this system are not available, some uncertainties, however, were left for further study.

IV. CONCLUSION

In summary, XPS and UPS measurements on BaV$_{1-x}$Ti$_x$S$_3$ with $x = 0$ and 0.2 were performed. The XPS results indicate that the valence of V as well as Ti is not 4 as would be expected nominally, but in between 3 and 4. Essentially no difference of the core-level binding energies was observed between the two samples. There are three peak features in the valence band from the UPS measurements. It is concluded from the enhancement by the He II photon that V $3d$ orbitals are incorporated in the peak feature at 1 eV. It was shown that the bond-valence-sum method seems to be useful as a quantitative tool for discussion of XPS results. Further possibility of using the BVS for discussion in relation with the transport properties of the system was also shown.

Finally, it is noted that since the electronic structure of this system changes drastically below 70 K, investigation of the photoelectron spectra below this temperature in comparison with this study would be of great interest.

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[19]This is very close to the V-V distance between atoms in vanadium metal of 2.61 Å.