Large entropy change derived from orbitally assisted three-centered two-electron σ bond formation in metallic Li_{0.33}VS₂

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We discuss herein the emergence of a large entropy change in metallic $Li_{0.33}VS_2$ derived from orbitally assisted loose σ bond formation. Comprehensive structural studies based on synchrotron x-ray and neutron diffraction analyses clarify the fabrication of ribbon chains at 375 K, consisting of multiple three-centered two-electron σ bonds based on the viewpoint of local chemical bonding. Although the metallic conductivity persists down to the lowest temperature measured, an exceptionally large entropy change as a metal, as much as $\Delta S = 6.6 \text{ J mol}^{-1} \text{ K}^{-1}$, appears at the transition. The emergence of a large entropy change in a metallic state may possibly lead to different functional materials, such as a heat-storage material with a rapid thermal response.

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The search for various self-organizing phenomena in which multiple degrees of freedom of electrons intertwine in solids has been intensively studied. Examples include stripelike charge ordering in copper and nickel oxides [1], and the spontaneous formation of various molecular clusters in lowdimensional and/or geometrically frustrated systems [2–9]. The driving force of the latter example is the formation of molecular orbitals accompanied by a periodic modulation of the lattice structure, which gives rise to strong metal-metal bonds between the adjacent transition-metal ions.

The variety of molecular cluster patterns is strongly related to the number of *d* electrons. In d^1 -electron systems, dimers usually form between adjacent transition-metal ions; MgTi₂O₄ with a spinel lattice is an example [3]. For d^2 -electron systems, triangular-shaped trimers appear, as demonstrated by LiVO₂ and LiVS₂, which have two-dimensional triangular lattices [4,10,11]. When a noninteger number of *d* electrons is involved in the bonds, complicated cluster patterns appear, such as for the octamer in CuIr₂S₄ [6]. Although the cluster patterns vary, the mechanism of the cluster formation can be generally understood based on the concept of an orbitally induced Peierls state, proposed by Khomskii and Mizokawa [12]. From the viewpoint of local bonding, the resulting clusters consist of multiple dimers with two-centered two-electron σ bonds (2*c*-2*e*) [2–9].

For a two-dimensional triangular lattice system with a *d*-electron number of 4/3, ribbon chains of one-dimensional clusters consisting of multiple linear trimers appear [13]. The examples include MTe_2 (M = V, Nb, Ta), as we will describe in detail later [14,15]. Whangbo *et al.* proposed

that the ribbon chain formation can be understood based on the concepts of both hidden one-dimensional Fermi-surface nesting in d orbitals connected to form a one-dimensional chain and local chemical bonding [13]. Although the former is basically consistent with the orbitally induced Peierls state introduced above [12], the resulting local bonds constituting linear trimers can be interpreted as a loose three-centered two-electron σ bond (3*c*-2*e*), which sharply differs from the tight 2c-2e bond [2–9]. Considering that various physical properties and functions derived from bonding are central themes in condensed matter physics [16, 17], such as the control of magnetism [18], the anomalous metallic state [4,9,19], and bond breaking superconductivity [7,20], experimental investigations of loose 3c-2e bonds should extend the possible methodologies, leading to the chances of obtaining different functional materials.

In this Rapid Communication, we present the crystal structure and properties of the layered transition-metal dichalcogenide $\text{Li}_{0.33}\text{VS}_2$, which, upon cooling, undergoes a trigonalto-monoclinic phase transition accompanied by ribbon chain formation consisting of multiple 3c-2e bonds. We show that the entropy of $\text{Li}_{0.33}\text{VS}_2$ changes by as much as $\Delta S =$ $6.6 \text{ J mol}^{-1} \text{ K}^{-1}$ at the transition, although it has high electrical conductivity down to the lowest temperature measured. We discuss that the exceptionally large entropy change in a metallic state is derived from orbitally assisted loose 3c-2e bond formation, possibly leading to different functional materials, such as heat-storage materials with a rapid thermal response.

Powder samples of $Li_{0.33}VS_2$ were prepared using a softchemical method followed by a solid-state reaction. Initially, Li-deficient $Li_{\sim 0.75}VS_2$ was obtained by reacting an appropriate amount of Li_2S , V, and S in an evacuated quartz tube at 700 °C for 3 days. The products were immersed

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in a 0.2M n-BuLi hexane solution for 2 days to obtain LiVS₂. Next, the Li content was quantitatively tuned to obtain $Li_{0.33}VS_2$ by using an I_2 acetonitrile solution, by using the equation $LiVS_2 + 0.33I_2$ $Li_{0.33}VS_2 + 0.67LiI$. The samples were characterized by both neutron and synchrotron powder x-ray diffraction experiments. Neutron diffraction experiment was done by using ~ 10 g of powdered samples in iMATERIA beamline equipped at J-PARC, Japan [21]. For analysis, the Z-RIETVELD software [22,23] was used. Synchrotron powder x-ray diffraction experiments were done at BL5S2 beamline at Aichi Synchrotron, Japan. RIETAN-FP software [24] was employed for the Rietveld analysis. Differential scanning calorimetry (DSC) was conducted by using DSC 204 F1 Phoenix (Netzsch). Magnetic susceptibility was measured by a superconducting quantum interference device (SQUID) magnetometer (Quantum Design). The electrical resistivity was measured using the four-probe method. A first-principles calculation was performed using the WIEN2K code [25]. The computational details are available in the Supplemental Material [26].

Figures 1(a)-1(c) show the temperature dependence of the magnetic susceptibility, electrical resistivity, and DSC signals, respectively, for $Li_{0.33}VS_2$. This material is reported to undergo a first-order transition with a decrease in magnetic susceptibility at 375 K [27]. The present data show a similar temperature dependence, as shown in Fig. 1(a). The results of the neutron diffraction experiment show no sign of magnetic ordering at 200 K, as shown in the inset of Fig. 1(a). The magnetic susceptibility increases slightly at the lowest temperature, which may be attributed to paramagnetic impurities at concentrations below 1%. To measure electrical resistivity, we used a low-temperature sintered body, because the interlayer Li ions are easily defected when the sample is sintered at high temperature. Increasing the temperature through the phase transition at 375 K leads to a jump in the electrical resistivity; the low-temperature phase maintains a metallic conductivity of several m Ω cm. Considering that a low-temperature sintered sample is used, the intrinsic electrical resistivity is empirically one order of magnitude lower, indicating that $Li_{0.33}VS_2$ is metallic over the entire temperature range. Therefore, both phases above and below 375 K are Pauli paramagnetic phases, so the jump in magnetic susceptibility at the transition should be attributed to the difference in the electronic density of states. The electrical resistivity measurements also show anomalies at 294 K, which appear in all measured samples. However, the origin of the anomaly is unclear because no anomalies appear at the corresponding temperature in other experiments, such as magnetic susceptibility, DSC, and structural analysis, maybe indicating the anomaly is derived from the surface effect.

As shown in Fig. 1(c), the DSC experiment clarifies that a huge change in entropy of $\Delta S = 6.6 \text{ J mol}^{-1} \text{ K}^{-1}$ is accompanied by a first-order phase transition at 375 K. While the large entropy change often appears in localized electron systems, such as in LiVS₂ with $\Delta S = 6.4 \text{ J mol}^{-1} \text{ K}^{-1}$ and in LiVO₂ with $\Delta S = 14.5 \text{ J mol}^{-1} \text{ K}^{-1}$ [4], the entropy change of $\Delta S = 6.6 \text{ J mol}^{-1} \text{ K}^{-1}$ is extremely large for a metal-to-metal electronic phase transition, indicating the unusual feature of the transition in Li_{0.33}VS₂. Assuming that Li_{0.33}VS₂ is a metal weakly correlated with a Wilson ratio $R_W \sim 1$ in the whole temperature range, which gives an estimate of the maximum



FIG. 1. (a) Magnetic susceptibility of $Li_{0.33}VS_2$. Magnetic susceptibility data reported by Murphy *et al.* are taken from Ref. [27]. The inset shows the Rietveld refinement of neutron diffraction data at 200 K. Although a small impurity peak appears (see the asterisk), magnetic Bragg peaks are absent. (b) Electrical resistivity of $Li_{0.33}VS_2$. Because a large change in volume occurs at the transition at 375 K, cracks are generated in the sintered body, and the electrical resistivity as a function of temperature upon cooling does not match that upon heating. Only the cooling process is shown in (b). (c) DSC of $Li_{0.33}VS_2$. The inset shows the differentiated DSC data. No anomaly appears around 294 K.

entropy change as opposed to assuming other values for R_W , we can roughly estimate the entropy change to be $\Delta S = \Delta \gamma T_c \sim 1.5 \text{ J mol}^{-1} \text{ K}^{-1}$. It is extremely small compared with the experimental value of $\Delta S = 6.6 \text{ J mol}^{-1} \text{ K}^{-1}$, which seems to indicate that the transition involves ordering of the degrees of freedom, such as orbital.

To clarify the ground state of the low-temperature phase based on the structural analysis, we made comprehensive neutron and synchrotron x-ray diffraction studies. The neutron diffraction experiment indicates a Li fraction of 0.3388(13), which is very close to 1/3. The neutron diffraction experiment also clarifies that magnetic Bragg peaks do not emerge at the 375-K transition, as discussed before. An analysis of the synchrotron x-ray diffraction data gives the structural parameters at each temperature. As shown in Fig. 2(a), the high-temperature phase is refined as $P\bar{3}m1$ with a regular V triangular lattice. Although ~4.5% of the Li_{0.5}VS₂ impurity is identified, it is successfully corefined with Li_{0.33}VS₂. As shown in the inset of Fig. 2(a), the spectrum drastically changes below the transition temperature, and the low-temperature phase is



FIG. 2. Synchrotron x-ray diffraction data at (a) 400 K and (b) 370 K. The inset of (a) shows the spectrum around 375 K. The inset of (b) shows the spectrum around 294 K. No significant change appears corresponding to the anomaly observed in the resistivity measurements.

refined by using the monoclinic space group C2/m, as shown in Fig. 2(b). Table SI in the Supplemental Material summarizes the structural parameters [26].

Figures 3(a) and 3(b) show the low-temperature crystal structure obtained from the Rietveld analysis. At 375 K, Li ordering appears to form a one-dimensional chain in the



FIG. 3. (a), (b) Refined crystal structure of $Li_{0.33}VS_2$. A_L , B_L , and C_L indicate the V1-V1, V1-V2, and interchain V2-V2 bond lengths, respectively. Ribbon chains are clearly apparent in (b). (c) V-V bond length as a function of temperature.

direction of the *b* axis. In the low-temperature phase, the V site splits into two sites, V1 and V2 in a ratio of 1:2. As shown in Fig. 3(b), the V1 sites form a one-dimensional chain in the direction of the *b* axis, whereas V2 approaches the one-dimensional V1 chain. The result is that the ribbon chain in the low-temperature phase is clearly apparent. Figure 3(c) shows the temperature dependence of V-V distances. The distance A_L between adjacent V1 sites remains essentially constant across the transition, whereas the V1-V2 distance B_L within the ribbon chain decreases to 3.075 Å at 360 K, which is about 8% shorter than the V-V distance C_L is significantly increased.

The mechanism at work in the phase transition may be understood by invoking Whangbo's theory [13]. In the hightemperature phase, the xy, yz, and zx bands constructed by the corresponding d orbitals are 4/9 filled. The yz and zx onedimensional chains undergo a Peierls transition accompanied by a trigonal-to-monoclinic transition, which also broadens the yz and zx bands. As a result, the filling of yz and zx bands increases up to 2/3, forming linear trimers consisting of 3c-2e bonds. In contrast, the xy band becomes almost empty. The change in band filling, aided by Li-ion ordering, may be responsible for a large change in entropy of $\Delta S =$ $6.6 \text{ J} \text{ mol}^{-1} \text{ K}^{-1}$. Although the contribution of the Li-ion order to the change in entropy is not clear, we consider it to be negligibly small based on previous studies of the surrounding materials [28,29].

A characteristic Fermi surface to bolster this argument is realized by a first-principles calculation. As shown in Fig. 4(a), the Fermi surface at high temperature facilitates a good nesting feature with $Q = a^*/3$, which corresponds to the lattice periodicity in the low-temperature phase. Although Li ions one-dimensionally aligned parallel to the ribbon chain lead us to suspect that Li-ion ordering is a possible driving force behind the phase transition at 375 K, this is not the case. To support this claim, we assume a $3 \times 1 \times 1$ supercell, and structurally optimized the system using the virtual crystal approximation (VCA) scheme, whereby Li ions are uniformly aligned. The result indicates that the ribbon chain structure actually reduces the ground-state energy and yields bond lengths near the experimental lengths $A_L = 3.28, B_L = 3.06$, and $C_L = 3.73$. This means that the instability towards the ribbon chain structure is inherent in the electronic state of the two-dimensional VS₂ plane and the observed Li-ion ordering is merely a consequence of ribbon chain formation.

We should note that there are some tellurides, $M\text{Te}_2$ (M = V, Nb, Ta), which exhibit structural phase transitions from a regular triangular lattice with trigonal symmetry to monoclinic with the formation of ribbon chains upon cooling [13–15]. It is discussed that the Te *p*-block bands increase in energy because of the interlayer Te-Te interactions, thereby leading to a partial electron transfer from the top portion of the Te *p*-block bands to the *d*-block bands of the metal, resulting in the actual $d^{4/3}$ electron count and following 3c-2e bond formation. However, the present Li_{0.33}VS₂ should be more appropriate than these tellurides for investigating the intrinsic nature derived from loose 3c-2e formations for some reasons. Initially, the formal *d* electron count for vanadium can be finely tuned to 4/3 in Li_{0.33}VS₂. The diffraction study clearly shows that the



FIG. 4. (a) Fermi surface in the high-temperature phase of $Li_{0.33}VS_2$. Partial density of states in (b) high- and (c) low-temperature regions. (d) Three molecular orbitals derived accompanied by the 3c-2e formation. Schematic view of band structures originating from d_{xy} , d_{yz} , and d_{zx} orbitals at (e) high and (f) low temperatures.

interlayer S-S distance of 3.788 Å at 400 K is significantly longer than the sum of the van der Waals radii of the S²⁻ ion [30], which means that the interlayer p-p hybridization is negligibly small compared with these tellurides. In turn, this indicates that the d electronic state can be finely tuned by controlling the Li fraction. The neutron diffraction result indicates that the Li fraction is quite close to 1/3, which ensures the presence of a $d^{4/3}$ electronic state in Li_{0.33}VS₂. Second, we can expect weak p-d hybridization in Li_{0.33}VS₂, which is compared with the strong p-d hybridization inherent to 1T tellurides [31]. The previous band calculations clearly indicate the considerable contribution of a Te 5p character at the Fermi level [32], which prevents us from studying the intrinsic nature of the 3c-2e state derived from a strong d character. In Li_{0.33}VS₂, the first-principles calculation clearly indicates a negligibly small p-d hybridization. As shown in Figs. 4(b) and 4(c), the S 3 p band is completely separated from the V 3d band in both the high- and low-temperature phases, and the strong V 3d character dominates near the Fermi energy.

The calculation further clarifies the modification of the band structure derived from the 3c-2e formation. As shown schematically in Fig. 4(e), the xy, yz, and zx bands are triply degenerated at high temperatures. Thus, we expect the yz and zx bands to transform into bands composed of three components at a low temperature: bonding, nonbonding, and antibonding, as shown in Fig. 4(d). We thus divide the yz and zx bands into three parts, as shown in Fig. 4(f). Whereas the bonding orbitals are almost filled, the Fermi surface survives due to the small stabilization energy of the bonding orbital

following the incomplete gap opening between the bonding and nonbonding orbitals, and the overlap between the yz and zx bands, with the xy band further generating a small charge transfer between them. The existence of the Fermi surface is consistent with the metallic conductivity observed in the resistivity measurement.

The metallic conductivity at low temperatures differs sharply from the insulating behavior observed in conventional molecular cluster compounds with 2c-2e bonds [2–9]. The reason is strongly related to the bonding nature. For example, LiVS₂, which is the d^2 analog of Li_{0.33}VS₂, undergoes a metal-to-insulator transition at 314 K, accompanied by the formation of V triangular-shaped trimers consisting of multiple 2c-2e bonds [4]. The change in V-V distance reaches \sim 12% at the transition in LiVS₂, whereas the V-V distance is 3.39 Å at high temperatures and the intratrimer V-V distance decreases to 2.997 Å at low temperatures [4]. The $\sim 12\%$ change in the V-V distance is much greater than the $\sim 8\%$ change in $Li_{0,33}VS_2$, which indicates that the 2c-2e bond is much stronger than the 3*c*-2*e* bond, as can be understood intuitively. Because the bond strength is a function of the band gap, we consider that the weakness of the 3c-2e bond may be explained by the incomplete gap, leading to the metallic conductivity in the low-temperature phase of Li_{0.33}VS₂. Conversely, however, a large change in entropy of $\Delta S = 6.6 \text{ J} \text{ mol}^{-1} \text{ K}^{-1}$ at the transition in Li_{0.33}VS₂ seldom appears in conventional itinerant electron systems, such as 2H-TaSe₂ and 4Hb-TaSe₂ [33], which frequently appear in compounds in which molecular clusters form, accompanied by orbital ordering [4,34-36]. The coexistence of high electrical conductivity and a large change in entropy is a remarkable feature of $Li_{0.33}VS_2$ with 3c-2ebonds, which sharply differs from that for 2c-2e bonds, leading to different functional materials.

One possible application is as a heat-storage material with a rapid thermal response. Many conventional heat-storage materials exploit a large change in enthalpy in the solid-liquid phase transition, such as paraffin with $140 \,\mathrm{J}\,\mathrm{cc}^{-1}$ at a melting point m.p. = $64 \degree C$ [37] and polyethylene glycol with 165 J cc⁻¹ at m.p. = $20 \circ C$ [38]. Heat-storage materials that exploit a solid-liquid phase transition have a large enthalpy, whereas a low thermal conductivity leads to a difference between the internal temperature and the surface temperature, making it difficult to keep the surface temperature constant. Thus, fabricating heat-storage materials that exploit a solid-solid phase transition is strongly desired, and attention has focused on heat-storage materials that exploit the enthalpy change that is accompanied by an electronic phase transition in strongly correlated electron systems [39-42]. Our estimate gives an enthalpy change $\Delta H = 73.1 \text{ J} \text{ cc}^{-1}$ for Li_{0.33}VS₂, which is derived from $\Delta S = 6.6 \text{ J mol}^{-1} \text{ K}^{-1}$. This is a relatively large value for a heat-storage material that exploits a solid-solid transition, as summarized in Table SII in the Supplemental Material [26]. Note that the high electrical conductivity, which is a feature of Li_{0.33}VS₂, improves the thermal conductivity and leads to a rapid thermal response. This characteristic is unique to Li_{0.33}VS₂ and is not found in conventional heat-storage materials that use the solid-solid phase transition. Thus, the 3c-2e bond is an interesting topic for both basic and applied sciences.

To summarize, we present physical and structural studies of the layered two-dimensional triangular lattice

system Li_{0.33}VS₂, and discuss how Li_{0.33}VS₂ embodies the 3c-2e bond. Compared with a conventional 2c-2e bond, the 3c-2e bond is loose, which leads to an incomplete band gap and concomitant metallic conductivity at low temperatures. In contrast, the entropy change at the transition is exceptionally large as a metal. The coexistence of these features may make Li_{0.33}VS₂ a useful functional material.

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