Metal-insulator transition and optical conductivity in BaVS$_3$

Arata Tanaka  
Department of Quantum Matter, ADSM, Hiroshima University, Higashi-Hiroshima 739-8530, Japan  
E-mail: atanaka@hiroshima-u.ac.jp

Abstract. Possible orbital orders below the metal-insulator transition temperature in quasi-one-dimensional BaVS$_3$ have been investigated in relation to the monoclinic lattice distortion in the insulating phase using a one-dimensional two-band Hubbard model. Orbital occupations in the ground state and optical conductivity have been calculated by means of exact diagonalization of finite size clusters. Depending on the size of crystal field splitting of the $t_{2g}$ levels, two different orbital orders in the $t_{2g}$ orbitals with the periodicity of four V ion sites along the $c$-axis are found to be stabilized with the lattice distortion. The on-site exchange interaction plays important role in the formation of these orbital orders.

1. Introduction  
Quasi-one-dimensional BaVS$_3$ has the hexagonal perovskite structure, in which the face-sharing VS$_6$ octahedrons form linear chains of V ions along the $c$-axis. It exhibits three successive second order phase transitions, whose origin are still controversial. A hexagonal to orthorhombic structural transition occurs at $T_S = 240$ K, where the V ion chains become zigzag chains. A metal-insulator transition (MIT) at $T_{MI} = 70$ K is accompanied by a monoclinic distortion doubling the unit cell with four different V ion sites along the chain. An incommensurate magnetic ordering occurs below $T_X = 30$ K. The $t_{2g}$ level of each of V ions is split into doubly degenerated $e_g^\pi$ and single $a_{1g}$ levels by a small trigonal field. Both the $a_{1g}$ orbitals with one-dimensional character forming wide bands and the $e_g^\sigma$ orbitals with their lobes towards interchain directions forming narrow bands contribute the states near the Fermi level [1]. This $t_{2g}$ orbital degree of freedom is considered to play important role in MIT. The formations of charge and orbital orders [2, 3, 4] and a spin-orbital liquid [5] have been proposed for the origin of MIT.

2. Model and Methods of Calculations  
To elucidate the 3$d$ electronic state of the V ion chain across MIT in connection with the $t_{2g}$ orbital degeneracy and the monoclinic lattice distortion, a linear-chain two-band Hubbard model consists of eight sites with periodic boundary condition is considered. Since the degeneracy of the $e_g^\pi$ level is lifted by the orthorhombic lattice distortion below $T_S$, the lowest two $t_{2g}$ orbitals, the $a_{1g}$ and one of the $e_g^\pi$ orbitals, are taken into account in this model. The Hamiltonian of the
The optical conductivity has been calculated using the method in Ref. [8]. The optical conductivity with the electric polarization vector along the chain as a function of photon energy \( \omega \) can be described as

\[
\sigma_{zz}(\omega) = D_W \delta(\omega) + \frac{e^2}{N_\pi \omega} \text{Im} \left[ \langle g | j_z \frac{1}{H - E_g - \omega - i\delta} | g \rangle \right],
\]

where

\[
j_z = -i \sum_{l,m,m',\sigma} T_{l,m,m'} (c_{l+1,m,\sigma}^\dagger c_{l,m',\sigma} + c_{l,m',\sigma}^\dagger c_{l+1,m,\sigma}).
\]

Table 1. V-V bond lengths \( R_l \) between sites \( l \) and \( l+1 \) at 40 K in Ref. [6] and hopping integrals \( T_{l,a,a} \) for insulating phase calculated using eq. 2.

| \( l \) | \( R_l (\text{Å}) \) | \( T_{l,a,a} (\text{eV}) \) |
|---|---|---|
| 1, 5 | 2.896 | -0.526 |
| 2, 6 | 2.941 | -0.492 |
| 3, 7 | 2.753 | -0.600 |
| 4, 8 | 2.806 | -0.605 |

The optical conductivity with the electric polarization vector along the chain as a function of photon energy \( \omega \) can be described as

\[
\int_0^\infty \sigma_{zz}(\omega) \, d\omega = -\frac{\pi e^2}{4N} \sum_{l,m,m',\sigma} T_{l,m,m'} \langle g | (c_{l+1,m,\sigma}^\dagger c_{l,m',\sigma} + c_{l,m',\sigma}^\dagger c_{l+1,m,\sigma}) | g \rangle.
\]
The energy and wave function of the ground state are calculated using the Lanczos method and $\sigma_{zz}(\omega)$ in eq. 3 is obtained by the recursion method.

3. Results and Discussions

![Figure 1](image1.png)

Figure 1. (a) $a_{1g}$ orbital occupation per site as a function of $D$ with (circles) and without (triangles) the effect of the monoclinic lattice distortion. (b) $a_{1g}$ (circles) and $e_{g}^a$ (triangles) orbital occupations of each site for $D = -0.4$ eV and $D = -0.24$ eV with monoclinic lattice distortion. The lines are drawn as guides for eyes.

Figure 1(a) shows the averaged occupation number of the $a_{1g}$ orbital over sites $\pi_a$ as a function of $D$ with and without the monoclinic lattice distortion. The $a_{1g}$ orbital occupation is increased steadily with increasing $D$ without the lattice distortion. However, the state with $\pi_a \sim 1/2$ and $\pi_a \sim 1/4$ are particularly stabilized with the lattice distortion. To examine these two states more closely, the $a_{1g}$ and $e_{g}^a$ orbital occupations in each site are presented in Fig. 1(b) for $D = -0.24$ eV with $\pi_a \sim 1/2$ and for $D = -0.4$ eV with $\pi_a \sim 1/4$. The patterns of the orbital order are different between these two states. The alignment $e_{g}^a-e_{g}^a-a_{1g}-a_{1g}$ is found with $D = -0.24$ eV, whereas $e_{g}^a-e_{g}^a-e_{g}^a-a_{1g}$ with $D = -0.4$ eV. While there are large variations in the orbital occupations among the sites, the disproportionation of the charge $n_{l,a} + n_{l,e}$ among the sites is small as discussed in the previous work [4].

The $a_{1g}$ orbital is preferably occupied at site 4, because of the strong $a_{1g}-a_{1g}$ hybridization to the neighboring site owing to short V-V distance (see table 1). This can be regarded as the effective $a_{1g}-e_{g}^a$ level splitting at site 4 is larger than the other sites and also implies that switching from the high-spin $S = 1 (a_{1g})^1(e_{g}^a)^1$ configuration to the low-spin $S = 0 (a_{1g})^2$ configuration occurs at smaller $D$ than the other sites when the site is doubly occupied. The orbital and spin correlations between site 4 and the neighbors are strongly depend on the electronic configuration of the $d^2$ state of site 4 created by charge fluctuation. For small $D$, the high-spin $(a_{1g})^1(e_{g}^a)^1$ configuration at site 4 is preferred and this induces the $a_{1g}-e_{g}^a$ orbital order with ferromagnetic spin correlation between site 4 and the neighbors. Similarly, the $a_{1g}-e_{g}^a$ orbital order with antiferromagnetic spin correlation are expected between site 4 and the neighbors for large $D$. In fact, the $e_{g}^a-a_{1g}-e_{g}^a$ orbital alignment of sites 3 to 5 and the ferromagnetic spin correlation of site 4 and the neighbors $\langle S_3 \cdot S_4 \rangle \sim \langle S_4 \cdot S_5 \rangle \sim 0.19$ with $D = -0.4$ eV are contrasted with the $a_{1g}-a_{1g}$ orbital alignment and the antiferromagnetic spin correlation $\langle S_3 \cdot S_4 \rangle \sim -0.45$ between sites 3 and 4 with $D = -0.24$ eV. Similar high- to low-spin state switching at doubly occupied sites at MIT in VO$_2$ and Ti$_2$O$_3$ has been discussed [9].

To examine the effects of the monoclinic lattice distortion on the electric transport properties, in Fig. 2(a), the Drude weight $D_W$ as a function of $D$ calculated with and without the distortion are shown. The unphysical negative $D_W$ values are the result of the finite size effect and indicate insulating behavior of the system [8]. While such insulating behavior can be seen rather limited
Figure 2. (a) Drude weight $D_W$ as a function of $D$ with (circles) and without (triangles) the effect of the monoclinic lattice distortion. (b) Optical conductivity spectra for $D = -0.24$ eV with (upper panel) and without (lower panel) the effect of the monoclinic lattice distortion. (c) The same to (b) but for $D = -0.4$ eV.

The range of $D$ where the value of $\bar{\pi}_a$ is $\sim 1/2$ without distortion, much wider ranges of $D$ where the orbital orders $e^g_{a_g}e^g_{a_{1g}} \pm a_{1g}$ or $e^x_{a_g}e^x_{a_{1g}} \pm a_{1g}$ occur are insulating with the distortion. The sign of $D_W$ changes from positive to negative by including the effects of distortion in the ranges $-2.6 \text{ eV} \leq D \leq -2.4 \text{ eV}$, and $-4.8 \text{ eV} \leq D \leq -3.8 \text{ eV}$.

In Figs. 2(b) and 2(c), optical conductivity spectra calculated with $D = -0.24$ eV (b) and $D = -0.4$ eV (c) are shown. In the case of the spectra with $D = -0.24$ eV, the spectral weight distributed within $\omega < 2 \text{ eV}$ without the lattice distortion converges into a sharp peak located at $\omega \sim 0.8 \text{ eV}$ when the lattice distortion is considered. On the other hand, although large spectral weight transfer to the Drude peak can be seen, no such drastic change in the intensity of the peak at $\omega \sim 1.2 \text{ eV}$ is found for the spectra with $D = -0.4$ eV. This is consistent with the fact that no clear change in the intensity of a peak centered around $\omega \sim 1.2 \text{ eV}$ is found across MIT in experimental spectra with the polarization vector parallel to the $c$-axis [10].

4. Conclusions

Possible orbital orders below $T_{\text{MI}}$ and the optical conductivity are investigated as a function of the $e^g_{a_g} \pm a_{1g}$ level separation. States having small Drude weights with orbital alignments $e^x_{a_g}e^x_{a_{1g}}$ and $e^g_{a_g}e^g_{a_{1g}}$ are particularly stabilized when the effects of the monoclinic distortion is considered. The on-site exchange interaction plays important role in the formation of these orders. From these findings, it is inferred that the MIT is caused by the orbital order stabilized by the strong electron-lattice coupling.

References

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