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# Design of a $d^1$ -analogue of cuprates: $\text{Sr}_2\text{VO}_4$ and $\text{Ba}_2\text{VO}_4$ under pressure

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## Abstract

By means of a combination of the local density approximation and dynamical mean field theory (LDA + DMFT), we study the possibility of making a  $d^1$  analogue of  $d^9$  cuprates on the basis of  $\text{Sr}_2\text{VO}_4$ . We calculate the electronic structure of  $\text{Sr}_2\text{VO}_4$  under pressure, and show that while the material is a 1/6-filled three-band system at ambient pressure with a small level splitting between the  $d_{xy}$ - and  $d_{yz/zx}$ -bands, an orbital polarization occurs under sufficiently high uniaxial pressure in the  $c$ -direction. While all energy scales are relatively small, the electronic structure of  $\text{Sr}_2\text{VO}_4$  under pressure is similar to that of  $\text{La}_2\text{CuO}_4$ ; it is a two-dimensional half-filled single-band system which has, relative to the nearest neighbour hopping, a similar Coulomb repulsion and next-nearest neighbour hopping. We also study the effect of substituting Sr by Ba, i.e., chemical pressure, and show that the pressure needed for the orbital polarization is considerably reduced.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

While twenty years have passed since the discovery of high  $T_c$  (transition temperature) superconductivity in cuprates [1], we still do not have any other superconducting transition metal oxides with a  $T_c$  as high as that of cuprates. If there were another high  $T_c$  material, it would certainly provide useful information to clarify the mechanism of high- $T_c$  superconductivity.

In fact, up to present, there have been several attempts to synthesize transition metal compounds which have an electronic structure similar to that of cuprates. For example, we can consider making a 4d analogue of cuprates.  $\text{A}_2\text{AgF}_4$  ( $\text{A} = \text{Na}, \text{K}, \text{Cs}$ ) is a possible candidate,

in that it has the same crystal structure as  $\text{La}_2\text{CuO}_4$ ; La, Cu, and O are replaced by an alkali metal, Ag, and F, respectively.

However, while the distance between apical O and Cu is much larger than that in the  $ab$ -plane in  $\text{La}_2\text{CuO}_4$ , that between apical A and Ag of  $\text{A}_2\text{AgF}_4$  is even smaller than the in-plane A–Ag distance. Therefore, as is shown by the recent LDA (local density approximation) calculation for  $\text{Cs}_2\text{AgF}_4$  [2], the  $4d_{3z^2-r^2}$  level is higher in energy than the  $4d_{x^2-y^2}$  level, whereas the  $3d_{x^2-y^2}$  orbital is much higher than the  $3d_{3z^2-r^2}$  in the case of cuprates. Experimentally, not superconductivity but ferromagnetism is observed in these compounds.

Another possible approach to realize an electronic structure similar to that of cuprates is to look for its  $3d^1$  analogue. In fact,  $\text{Sr}_2\text{VO}_4$  has attracted much interest in this context. It can be regarded as an interesting ‘dual’ material of  $\text{La}_2\text{CuO}_4$ , because  $\text{Sr}_2\text{VO}_4$  has one electron per V ion, while  $\text{La}_2\text{CuO}_4$  has one hole per Cu ion. However, as was shown in the early LDA calculation [3], the level splitting of  $t_{2g}$  in  $\text{Sr}_2\text{VO}_4$  is much smaller than that of  $e_g$  in  $\text{La}_2\text{CuO}_4$ , so that  $\text{Sr}_2\text{VO}_4$  is not a half-filled single band system but a 1/6-filled three-band ( $d_{xy/yz/zx}$ ) system. Results of recent beyond-LDA calculations also suggest that the relation between  $\text{Sr}_2\text{VO}_4$  and  $\text{La}_2\text{CuO}_4$  is not dual [4, 5]. In particular, Imai *et al* carried out an LDA + PIRG (path integral renormalization group) calculation and found a nontrivial orbital-stripe order [4]. These orbital degrees of freedom are irrelevant in cuprates. Hence, maybe not surprisingly, experiments also show that  $\text{Sr}_2\text{VO}_4$  and  $\text{La}_2\text{CuO}_4$  behave differently. For example, finite ferromagnetic moments are observed for  $\text{Sr}_2\text{VO}_4$  [6].

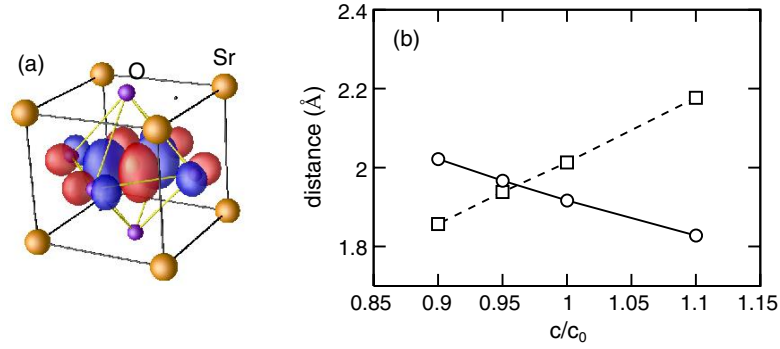
Therefore, it has not been possible to synthesize any analogue of cuprates so far. In this paper, we will point out a possible path to design such an analogue; if we distort the  $\text{VO}_6$  octahedron by applying sufficiently high uniaxial pressure we can control the level splitting of the d levels. As we will show by means of the LDA + DMFT method [7, 8], an electronic structure similar to that of cuprates can then be realized. The reason why we focus on  $\text{Sr}_2\text{VO}_4$  is that one of the authors and his coworkers [9] have quite recently succeeded in growing a thin  $\text{Sr}_2\text{VO}_4$  film by means of epitaxial growth techniques. Hence, in principle, we can consider applying pressure to  $\text{Sr}_2\text{VO}_4$  in some specific direction. We indeed show below that if we apply uniaxial pressure in the  $c$ -direction,  $\text{Sr}_2\text{VO}_4$  can become a  $d^1$  analogue of  $d^9$  cuprates, with very similar hopping and interaction parameters for the effective one-band Hubbard model. We also study the effect of chemical pressure and show that if we substitute Sr by Ba, the pressure needed to make a  $d^1$  analogue of  $d^9$  cuprates is considerably reduced.

## 2. GGA optimization of crystal structure

Let us start with the optimization of the atomic configuration. By means of GGA (generalized gradient approximation) calculation with plane-wave basis<sup>4</sup>, we first calculate the total energy of the system as a function of the lattice constant  $a$ , fixing the ratio  $c/a$  to its experimental value ( $=3.28$ ) [6]. We find that the energy minimum is at  $a = 3.89 \text{ \AA}$ , in excellent agreement with experiment ( $a = 3.84 \text{ \AA}$ ). When the lattice constant  $a$  is fixed to this optimized value, the Sr–V and O–V distances along the  $c$ -direction (see figure 1(a), which shows the  $\text{VO}_6$  octahedron), which are the only two free parameters to be optimized, become 4.46 and 2.01  $\text{ \AA}$ , respectively, consistent with the experimental values 4.46 and 1.98  $\text{ \AA}$ .

Next, we change the lattice constants to simulate the effect of pressure. By applying high uniaxial pressure or, more realistically, synthesizing  $\text{Sr}_2\text{VO}_4$  films on substrates with appropriate lattice constants, here we change the lattice constant  $c$  up to  $\pm 10\%$  of the

<sup>4</sup> We employ the Tokyo *ab initio* Program Package (TAPP), see [10].



**Figure 1.** Atomic configuration of  $\text{Sr}_2\text{VO}_4$  together with the NMTO Wannier function of the V  $d_{xy}$ -orbital. The position of Sr and the apical oxygen are optimized by a plane-wave GGA calculation. (b) GGA-optimized distance between O and V along the  $c$  direction (open squares) and in the  $ab$ -plane (open circles) as a function of the  $c$  axis elongation  $c/c_0$ .

experimental value  $c_0 = 12.6 \text{ \AA}$ , fixing the volume of the unit cell. We assume that the system has the same  $I4/mmm$  symmetry as at atmospheric pressure<sup>5</sup>.

In figure 1(b), we show the GGA-optimized distance between O and V along the  $c$ -direction ( $d_c$ ) and within the  $ab$ -plane ( $d_{ab}$ ) as a function of  $c/c_0$ . We can see that while  $d_c$  is longer than  $d_{ab}$  at ambient pressure,  $d_c$  becomes shorter than  $d_{ab}$  for  $c/c_0 < 0.95$ .

### 3. NMTO downfolding

If  $d_c$  becomes sufficiently shorter than  $d_{ab}$ , we can expect that the  $d_{xy}$  level becomes lower in energy than the  $d_{yz/zx}$  level and orbital polarization might occur, i.e., a  $d^1$  analogue of cuprates can be realized. To examine this idea in the presence of electronic correlations, we perform LDA + DMFT calculations for the atomic configurations obtained above.

For DMFT calculations, we need an effective low-energy Hamiltonian. To obtain this, we perform LDA calculations with the LMTO (linearized muffin tin orbital) basis [11] and then carry out the NMTO ( $N$ th order muffin tin orbital) downfolding [12]. In figure 2, we plot the NMTO DOS (density of states) for  $c = 1.1c_0$  and  $0.9c_0$ , along with the band structure for ambient pressure ( $c/c_0 = 1$ ). Note, that the GGA calculation with plane-wave basis gives almost the same band structure (not shown).

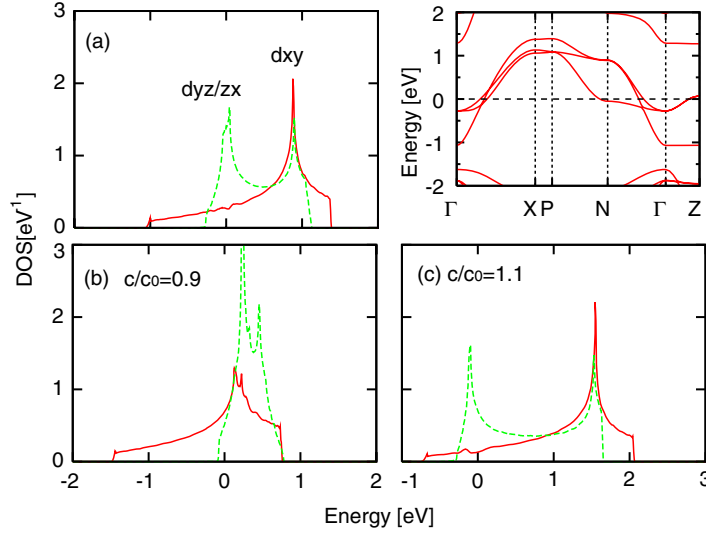
For the case of  $c/c_0 = 0.9(1.1)$ , figure 2 shows that the centre of gravity of the  $d_{yz/zx}$ -bands is clearly higher(lower) than that of the  $d_{xy}$ -band. Indeed, the crystal field splitting between the  $d_{xy}$ - and  $d_{xz/yz}$ -orbitals in the NMTO Hamiltonian is  $-382(+434)$  meV for  $c/c_0 = 0.9(1.1)$ . As for the electron occupation of the  $d_{xy}$ - and  $d_{xz/yz}$ -orbitals, while all three  $t_{2g}$  bands are similarly occupied for ambient pressure, 90% (20%) of the d electrons are accommodated in the  $d_{xy}$ -band for  $c/c_0 = 0.9(1.1)$  (see figure 3).

### 4. LDA + DMFT calculation

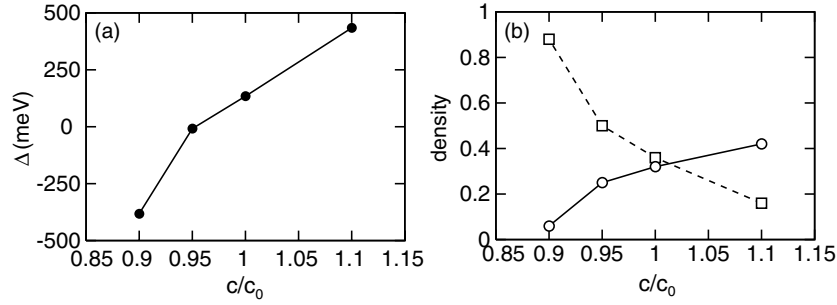
Next, we take into account the correlation effect. The Hamiltonian which we consider is

$$H = - \sum_{m,m'=d_{xy},d_{yz},d_{zx}} \sum_{i,j,\sigma} t_{mm'ij} \hat{c}_{im\sigma}^\dagger \hat{c}_{jm'\sigma} + U \sum_{i m \sigma} \hat{n}_{im\uparrow} \hat{n}_{im\downarrow} + \sum_{i;\sigma < \sigma'} (U' - \delta_{\sigma\sigma'} J) \hat{n}_{i1\sigma} \hat{n}_{i2\sigma'},$$

<sup>5</sup> Because of the large radius of the Sr ion, a significant tilting of the oxygen octahedra is not to be expected.



**Figure 2.** Density of states of the  $t_{2g}$  band for (a) atmospheric-pressure, (b) uniaxial pressure in the  $c$  direction ( $c/c_0 = 0.9$ ), and (c) uniaxial pressure in the  $ab$  plane ( $c/c_0 = 1.1$ ). The solid (dashed) line is for the  $d_{xy}$ -orbital ( $d_{yz/zx}$ -orbitals). Inset: LMTO band structure for atmospheric-pressure.

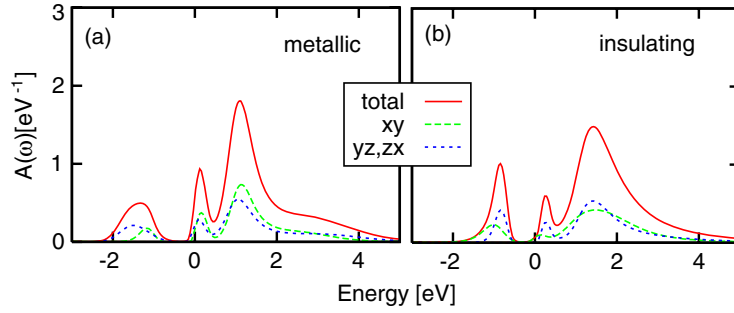


**Figure 3.** (a) NMTO crystal field splitting between the  $d_{xy}$ - and  $d_{xz/yz}$ -orbitals; (b) electron occupations for the  $d_{xy}$ - (squares) and  $d_{xz/yz}$ -orbitals (circles).

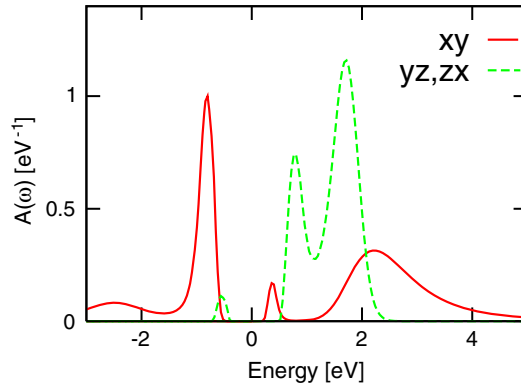
where  $\hat{c}_{im\sigma}^\dagger$  and  $\hat{c}_{im\sigma}$  are creation and annihilation operators for electrons on site  $i$  within orbital  $m$  and with spin  $\sigma$ , and  $t_{mm'ij}$  is the Fourier transform of the NMTO bandstructure for the  $t_{2g}$  orbitals. We employ the relation  $U = U' + 2J$  where  $U$ ,  $U'$ ,  $J$  are the intra-orbital Coulomb interaction, the inter-orbital Coulomb interaction and the Hund coupling, respectively. We solve this Hamiltonian within the framework of DMFT, by means of the standard Hirsch–Fye quantum Monte Carlo (QMC) method [13], where the temperature is 0.1 eV.

We first calculate the spectral function for ambient pressure with various interaction parameters  $U'$ , fixing  $J = 0.7$  eV. We find that while the spectral function is metallic for  $U' = 2.5$  eV (not shown), metallic and insulating solutions coexist for  $U' = 2.8$  (see figure 4), namely the Mott–Hubbard transition occurs around  $U' = 2.5$ – $2.8$ . Since the Mott gap in the insulating solution is in accord with the main optical peak in experiment [9], we expect  $U' \sim 2.8$  eV for  $\text{Sr}_2\text{VO}_4$ .

Let us now consider uniaxial pressure in the direction of the  $c$  axis. In figure 5, we plot the spectral function for  $c/c_0 = 0.9$ . Note, that the spectrum is now insulating, even for the smaller



**Figure 4.** LDA + DMFT spectral function for  $U' = 2.8$ , where dashed, dotted, and solid lines are for  $d_{xy}$ ,  $d_{xz/yz}$ , and the total  $\text{Sr}_2\text{VO}_4$  spectrum, respectively. Two solutions (metallic (a) and insulating (b)) coexist.



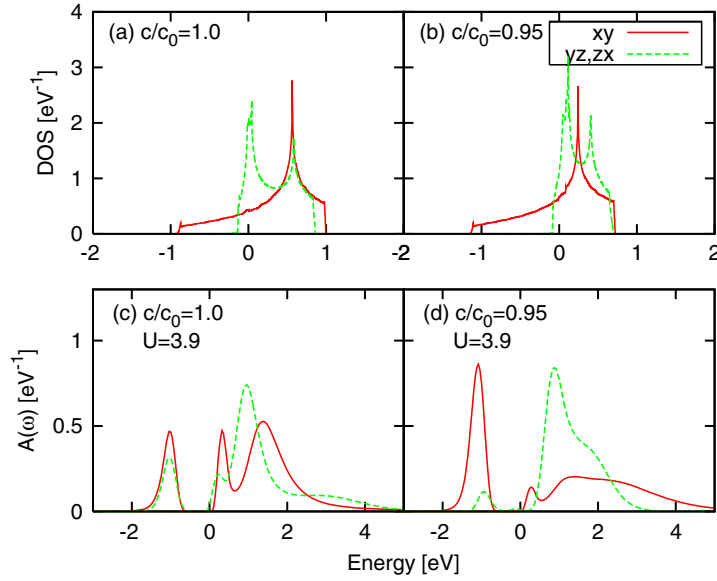
**Figure 5.** Same as figure 4 but for uniaxial pressure in the direction of the  $c$  axis ( $c/c_0 = 0.9$ ) with  $U' = 2.5$ .

value of  $U' = 2.5$  for which we have a metallic solution at ambient pressure. This is interesting since usually pressure makes an insulator metallic. Here, we have the opposite: pressure makes the system insulating.

This behaviour can be understood as follows. From figure 2, we see that the LDA bandwidth does not change strongly from 2.26 eV at  $c/c_0 = 1$  to 2.46 eV at  $c/c_0 = 0.9$ . This small change of bandwidth alone would indeed indicate more metallic behaviour as one would usually expect. But more important is that uniaxial pressure changes the crystal-field splitting; the two  $d_{yz/zx}$ -orbitals become almost unoccupied, and then the large intra-orbital repulsion  $U$  makes the remaining (single)  $d_{xy}$ -orbital Mott-insulating. That is, a  $d^1$  analogue of  $d^9$  cuprates is realized.

Here it is interesting to look at the energy scale of this effective one orbital ( $d_{xy}$ ) system. The NMTO effective Hamiltonian has a nearest neighbour hopping  $t = 0.26$  eV and next-nearest neighbour hopping  $t' = 0.06$  eV, which is comparable with those in the effective single-band Hubbard model for cuprates:  $t = 0.4$  eV,  $t' = -0.07$  eV and  $U = 5$  eV [16].

On the other hand, if we apply pressure in the  $ab$  plane, we find that the system is metallic for  $U' = 2.8$  and the  $d_{xy}$  band becomes almost empty (not shown). Therefore, the system is a quarter-filled two-band system, for which a strong tendency towards ferromagnetism is expected [14, 15].



**Figure 6.** Density of states of the  $t_{2g}$  band of  $\text{Ba}_2\text{VO}_4$  for (a) atmospheric-pressure and (b) uniaxial pressure in the  $c$  direction ( $c/c_0 = 0.95$ ). (c) and (d) are LDA + DMFT spectral functions for (a) and (b) respectively, with  $U' = 2.5$ .

## 5. Introduction of chemical pressure: $\text{Ba}_2\text{VO}_4$

While we have discussed the change of the electronic structure of  $\text{Sr}_2\text{VO}_4$  by controlling the lattice constant, it might be difficult to achieve a change of  $\pm 10\%$ . For example, when  $\text{Sr}_2\text{VO}_4$  is grown on a substrate this would result in an excessive lattice mismatch, which might result in a lattice relaxation. On the other hand, extrinsic uniaxial pressure applied on cuprates has not been more than 1 GPa so far [17].

Thus, lastly, we consider the possibility of chemical pressure by substituting Sr by Ba. By introducing Ba, we can expect that the crystal expands, because of the larger ion radius of Ba. Here, it is interesting to note that the V–O distance in the  $ab$  plane and that along the  $c$  axis will increase differently. Namely, while the increase of  $a$  directly affects the V–O distance in the  $ab$  plane (the latter is exactly half of the former),  $c$  and the V–O distance along the  $c$  axis are independent parameters.

To examine this idea, we perform GGA structure optimization for  $\text{Ba}_2\text{VO}_4$  by changing the  $a$  and  $c$  lattice constants, as in section 2. The energy minimum is at  $a = 4.04 \text{ \AA}$  and  $c/a = 3.36$ , where the V–O distances are  $2.02 \text{ \AA}$  (in the  $ab$  plane; compared to  $1.92 \text{ \AA}$  for  $\text{Sr}_2\text{VO}_4$ ) and  $2.01 \text{ \AA}$  (along the  $c$  direction,  $2.01 \text{ \AA}$  for  $\text{Sr}_2\text{VO}_4$ ), respectively. In fact, the situation for  $\text{Ba}_2\text{VO}_4$  is similar to that of  $\text{Sr}_2\text{VO}_4$  with  $c/c_0 = 0.95$ , i.e., for which a uniaxial pressure is already applied.

Let us now consider the compression of the  $c$  axis. As in section 3, after we obtain the optimized atomic configuration, we perform the NMTO downfolding for  $c/c_0 = 0.95$ . We find that the orbital polarization becomes larger, i.e., the electron density is 0.73 for the  $d_{xy}$  band and 0.14 for the  $d_{yz/zx}$  band.

Lastly, using the obtained NMTO Hamiltonian, we do a DMFT calculation. In figure 6, we plot the resulting LDA + DMFT spectral function for ambient pressure and uniaxial pressure in the  $c$  direction ( $c/c_0 = 0.95$ ) with  $U' = 2.5$ , along with the density of states by LDA. We

can see that large orbital polarization is realized even for  $c/c_0 = 0.95$ . Thus a  $d^1$  analogue of  $d^9$  cuprates can be realized more easily in  $\text{Ba}_2\text{VO}_4$  than in  $\text{Sr}_2\text{VO}_4$ .

## 6. Conclusion

In this paper, we have shown that we might be able to control the electronic properties of  $\text{Sr}_2\text{VO}_4$  by applying high uniaxial pressure. When the  $c$ -axis is elongated, only the  $d_{yz/yx}$ -bands are occupied,  $\text{Sr}_2\text{VO}_4$  becomes more metallic, and a ferromagnetic instability is to be expected. On the other hand, when the  $c$ -axis is compressed, the system will be more insulating, which can be regarded as an *inverse* Mott–Hubbard transition.  $\text{Sr}_2\text{VO}_4$  is then essentially a two-dimensional half-filled single-orbital system, and antiferromagnetic spin fluctuation should dominate. Hence we predict  $\text{Sr}_2\text{VO}_4$  to be a  $d^1$  analogue of  $d^9$  cuprates, with very similar hopping and interaction parameters for the effective one-band Hubbard model. If the Hubbard model is the fundamental microscopic model for superconductivity in cuprates, unconventional superconductivity should also be found in  $\text{Sr}_2\text{VO}_4$  under uniaxial pressure. We also study the effect of chemical pressure and show that if we substitute Sr by Ba, the pressure needed for orbital polarization is considerably reduced.

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